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ATMOSPHERIC HAZE: A REVIEW

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Submitted to:

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50 Moulton Street

Cambridge, Massachusetts 02138

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LIST OF SYMBOLS

A	Levine-Sedunov distribution functional
a, b, c	parameters in various empirical expressions
$D_{11}^{(L)}$	Gaussian dispersion in Sutton's formulas
E_1	electric field vector
$F_{1\ell}$	the scattering matrix
H	integral of collision
I	radiation intensity
K_{ij}	turbulent exchange coefficients
k	radiation wavenumber
L	horizontal distance
m	particle's relative refractive index
n	particle concentration
P	the Green function of the diffusion equation
p	degree of polarization

$R_{ii}^{(L)}$ Lagrange correlation functions of the wind velocity

r particle radius

S_i components of the Stokes vector

$T(\lambda)$ spectral transparency

t time

$tg\zeta$ ellipticity of polarization

u_1 average wind velocity

v velocity of sedimentation

x_j spatial coordinates of a particle

Z height above the ground

α Shifrin parameter

β index in the vertical distribution of turbulent exchange coefficients

γ extinction coefficient

δ_{ik}	Cronecker symbol
ϵ	dielectric constant
θ	scattering angle
κ	single-particle attenuation cross-section
λ	radiation wavelength
μ	micron
v	particle volume
ρ	Mie parameter
ρ_{ik}	radiation density matrix
σ_α	average density of the turbulent flux
Φ_1, Φ_2	rates of drop formation
χ	coefficient of molecular diffusion
ψ	orientation angle of the polarization ellipse

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I. INTRODUCTION AND OUTLINE OF FUTURE EFFORT

The recent acute interest in atmospheric hazes and associated aspects of air pollution reflects a general awareness of the threat of diminishing air resources. Because of the complexity of the problem which involves industrial, scientific, and biological, as well as social aspects, there is great dispersion of literature between these and other disciplines. In preparing this review we did not, therefore, aim at reviewing *all* the relevant publications; rather, the method was to identify the most important trends of haze research and to follow the development along these trends.

Most leading experts agree that the present state-of-the-art in haze research does not allow immediate formulation of a complete system for classifying and identifying various types of atmospheric haze. A further series of both laboratory and field studies appears necessary. If in the laboratory there is a tendency to consider simple systems which may not be readily relatable to the atmosphere, the object of field surveys, especially in urban regions, is so complex that the field studies rarely yield conclusive results. In view of this, the greatest importance should be attached to planning comprehensive complexes of identification measurements (combination of detailed direct analysis of aerosol samples with the scattering and transparency measurements, inclusion of the angular scanning techniques, polarization measurements, etc.).

In addition, there are more specific problems in each field of haze studies, the solution of which will be most helpful in improving the accuracy of any preliminary classification system.

The recommendations for each area of research are listed at the end of each chapter, in the order of priority.

In the field of atmospheric chemistry, it is necessary, first of all, to analyze and account for at least 30% of the mass of the

suspended particulate materials. This should be accompanied by further studies of the amount and the structures of carbon and organic compounds. Both laboratory and field analysis of sulfates and nitrates should be conducted in order to solve the problems of conversion and of smog formation. The possibility to obtain a quantitative evaluation of the relative role of antropogenic aerosol in natural hazes will depend on the work of field stations in different climatic locations, devoted to the analysis of physico-chemical composition of haze particles. It is obvious that chemical composition alone, even if obtained at the highest level of accuracy, is not sufficient to identify the haze origin. The data presented on Figs. 1 and 2 in this Report illustrate this statement: If in the range of large particles transition from continental to maritime aerosol is accompanied by the decrease of constituents sulfur, nitrogen, chlorine, in the range of giant particles, chlorine and sulfur content increases towards maritime atmospheres.

Therefore, a characteristic such as the size distribution of the haze particles appears to be a very important identification factor. Existing data on size distribution for the most part are related to very specific situations. It appears very desirable therefore to carry out a program of measuring the size distribution of particles in all possible types of hazes, according to the preliminary classification table (see p. 140). Organization of this and previously obtained material will depend on the success in theoretical prediction of the size distribution curve (see Chap. IV).

In the field of aerosol dynamics, the emphasis should be put on the accumulation of data on both temporal and spatial variation of pollutants concentration. The importance of measuring the temporal (diurnal and seasonal) cycles follows from the fact that

apparently only these could allow to distinguish between natural and antropogenic sulfates and nitrates (see Chap. IV). Besides, temporal variation of the size distribution together with relative humidity can help to separate the portion of particles that acts as condensation nuclei, thus yielding additional information on the chemical composition of aerosol.

The knowledge of the spatial distribution of air pollutant from a given source, depending on the state of the atmosphere (see Chap. V), is most important from the point of view of determining the source location. Once the problem is solved directly, we can predict typical seasonal and spatial patterns for each area, and any modification in this picture will mean introduction of a new source. Then a series of simultaneous measurements of the pollutant's concentrations in the vicinity of the source can indicate its intensity and nature. The success of this program will depend on the solution of inverse problem of turbulent diffusion.

Two lines of approach (solving the semiempirical equation of turbulent diffusion and constructing individual mathematical models for specific locations) should be pursued simultaneously.

In the field of atmospheric optics (see Chap. VI), the most important job is to develop identification techniques based on polarization measurements. Methods presently available (at a laboratory stage) make use of the total scattering cross-section. It is obvious that much more information can be obtained from the angular and spectral behavior of the scattering matrix. The main problem that arises here is the way of extracting this information. This will become more clear after solving certain mathematical problems in the theory of scattering, in particular, the problem of scattering by a nonspherical body.

From the point of view of the presently available information, the following set of physico-chemical measurements seems to be sufficient for a preliminary haze identification:

1. chemical composition
2. number concentration
3. weight concentration
4. size distribution (in the large particle range)
5. relative humidity.

Such characteristics as number and weight concentrations should be measured in terms of their diurnal cycles at least for two different seasons. This set is, of course, very labor and time consuming. Moreover, it implies simultaneous operation of many units of different equipment. Some of them, in the process of measurement, change the haze characteristics.

It appears very desirable therefore to develop an indirect approach that will allow faster measurements and will not interfere with the haze composition. Successes of optical instrumentation suggest to use scattering and transmission techniques to replace at least some of direct measurements.

As follows from the review of optical properties of aerosols (see Chap. VI, pp. 117-120), angular distribution of certain characteristics of the scattered light appears to be most valuable in terms of information content with respect to the scattering agent. In order to extract this information, both analytical and empirical approaches should be used. The solution of the direct problem will involve calculating the scattering characteristics for typical physico-chemical compositions of various hazes. This material can then be classified according to the sources of origin. Simultaneously, the measurements of appropriate polarization

characteristics with real hazes and laboratory aerosol systems, accompanied by detailed direct studies of physical and chemical composition, should be carried out. Then the matching of various air pollutants with their scattering patterns will form a basis for a fast and accurate identification method. It is hoped that accumulation of data on haze composition for areas with certain source patterns, together with their detailed optical analysis, will allow refinement of the initial classification scheme for measuring hazes and make it possible to formulate specific four-dimensional distributions of air pollutants, with the intent to make predictions of the pollution weather. After this, a complex of standard procedures for identifying each air pollution pattern should be formulated.

II. GENERAL DESCRIPTION OF HAZE COMPONENTS

Attenuation of light as it passes through the atmosphere is caused by three factors:

1. Rayleigh scattering by air molecules;
2. Selective molecular absorption;
3. Scattering and absorption by aerosol.

The Rayleigh scattering is relatively stable and exhibits a well-known spectral dependence $\sim \lambda^{-4}$.

Molecular absorption occurs on the molecules O_2 , H_2O , CO_2 , and O_3 . Earlier publications on this phenomenon date back to 1910 [235,58,215,212,207,290]; a more recent paper by Eldridge [69] contains a quantitative evaluation of the relative role of various components.

It is the presence of aerosols in various concentrations that leads to a variety of optical phenomena which change considerably from one place (and season) to another. Aerosols in the atmosphere form a suspended system with the size spectrum ranging from molecular clusters to particles of radius $r \sim 50\mu$. This spectrum results from a balance between coagulation, sedimentation, condensation, and other processes.

Approximate classification of atmospheric aerosol in terms of dust, smoke, or fog is based on origin considerations and is little indicative of the details of aerosol composition. The size spectrum is usually subdivided into three groups: Aitken nuclei ($r < .1\mu$), large particles ($0.1\mu < r < 0.6\mu$), and giant particles ($r > 1\mu$).

In order to avoid possible confusion that can be caused by the use of different concentration units, we want to point out

that in dealing with concentrations of a specific substance, usually gaseous, it is common to use the dimensionless mixing ratios of parts per million (ppm) and parts per billion (ppb). The choice between the two is merely for convenience to eliminate the use of many zeros in writing the numbers corresponding to the values of concentration. The mixing ratio is on a volumetric, or equivalently, a molecular ratio basis; e.g., a mixing ratio of 1 ppm for any substance implies that for every 10^6 molecules of gas there is one molecule of the substance.

The units of concentration for particulate material cannot usually be given in terms of a mixing ratio because the chemical composition is generally variable and often unknown. For this reason, concentrations of suspended particulate material are generally given in terms of mass per unit volume of air (or gas). In this Report we shall use the unit of microgram per cubic meter ($\mu\text{g} - \text{m}^{-3}$) or milligram per cubic meter ($\text{mg} - \text{m}^{-3}$). Again, the choice is merely for convenience in writing numerical values of the concentration.

The unit of length characterizing the size (radius) of a particle used in this Report is the micrometer (μm), formerly called the micron (μ).

If haze is determined as essentially an optical phenomenon associated with certain turbidity of the atmosphere, then it should be studied in close relation with optical properties of respective atmospheric constituents. In this sense the most important fraction of atmospheric aerosol is that of the size $0.1 - 0.3\mu$ (large particles), which is very difficult to measure directly and is most sensitive to variations of external factors. Usually particles in this range consist of Aitken nuclei dressed in water shells, or drops of solutions of various chemical composition.

Little information is available about their physico-chemical structure since practically any direct measurement leads to its partial destruction.

Processes of formation of Aitken nuclei include (1) condensation and sublimation of materials with low vapor pressures, (2) reactions between gaseous systems stimulated by heat or radiation, and (3) blowing up of material at the surface of earth or ocean.

The behaviour of an aerosol system depends to a great extent on the temporal and spatial structure of meteorological fields (wind, temperature, pressure, humidity, etc.). In the fluctuating velocity field of the atmospheric boundary layer, the main factor responsible for the dispersion of air pollutants is turbulent diffusion. The study of this phenomenon has resulted in an enormous amount of publications.

III. MECHANISMS OF HAZE FORMATION

A. Natural Aerosols

Aitken nuclei are ubiquitous in the troposphere, with the number concentrations at the surface over land about ten to one-hundred times larger than over the ocean. A practical definition of Aitken nuclei is particles with radii $< 0.1\mu$. Junge [151] estimated that the mean radius of Aitken nuclei is around $2-3 \times 10^{-2}\mu$, although there has been no direct observation of the shape of the size-frequency spectrum. Junge has reviewed the subject of origin and composition of Aitken nuclei; however, there have been no direct measurements of their composition because of the difficulty in obtaining samples free from larger particles.

Aitken nuclei result from:

1. Condensation and sublimation of materials with very low vapor pressures as in smokes from combustion processes. Forest fires and volcanoes are natural sources; man-made sources are numerous and may contribute most significantly, even in rural areas.
2. Reactions of trace gases through the influence of heat, light, or humidity. The combustion of NH_3 and HCl forms NH_4Cl in Aitken nuclei. (Other reactions with SO_2 which are thought possible will be discussed later.)
3. Dispersion by wind of mineral dust and sea spray.

On a global basis Aitken nuclei are primarily of continental origin. The composition of Aitken nuclei is thought generally to be similar to that of larger particles, although, for example, weathering processes may cause fractionation of rock and soil materials. It is generally considered that aerosols with number concentrations of the order of 10^4 cm^{-3} or less and with radii $< 10^{-1}\mu$ will not measurably obscure visibility.

Condensation nuclei in the atmosphere range in radius from a few hundredths of a micron to a few microns. However, most of the active condensation nuclei are in the size range $0.1 < r < 1\mu$. For the most part, atmospheric condensation nuclei play a significant role in limiting visibility by forming clouds of water droplets, or fogs, at the surface of the Earth. In that regard, it is important to know the composition of these condensation nuclei (CN). Junge [151] has reviewed and organized the main body of knowledge concerning physics and chemistry of aerosol particles and their role of water condensation. We will consider here a brief summary of the compositions and the relationship to visibility of the various types of aerosols, primarily as given by Junge.

Hazes of marine origin. The particles containing most of the mass of aerosol over the ocean are "giant particles" with radii $> 1\mu$. The composition of sea salt nuclei is virtually the same as that of sea water solute with respect to the main constituents, except that the nuclei are deficient in Cl. It is not clear how the Cl is released from the nuclei. Closer analyses of aerosols in various maritime atmospheres for the halogens Cl, Br, and I by Duce and Winchester *et al.* [62,63,64] indicate that Br and I are even more depleted than Cl. Sea salt nuclei exist in such small number concentrations over the oceans that they cannot play a significant role in the formation of cloud droplets. They may, however, be efficient initiators of raindrop formation in maritime clouds. The number concentrations of sea salt nuclei are generally less than 0.5 cm^{-3} for winds up to Beaufort force 7.

Maritime rainwater and sea-fog water analyses reveal compositions similar to those of sea salt nuclei. Srivastava and Ronne [319] observed cumulus clouds immersed in dense hazes over the Arabian Sea during the monsoon season in winds of force range 1-5

and with relative humidities of 80% -90%. They attempted to explain that the occurrence of the haze, in which the visibility was often less than 10 km, was caused by condensation of water vapor on sea salt particles. This explanation is at direct variance with Junge's conclusion and the data on concentrations of sea salt nuclei. A more consistent explanation of the hazes is that, at the high humidities, condensation nuclei of continental origin are blown over the sea and become active.

Continental aerosols. Aitken nuclei, though largely of continental origin, comprise a very small fraction of the mass of aerosol over land areas. In this regard, it is the "large" particles, those with $0.1 < r < 1.0\mu$, which predominate.

Analyses of residues of sea fog and cloud droplets in Japan by Kuroiwa [168,169], Yamomoto and Ohtake [378], and Isono [145] by means of electron microscopy and electron diffraction revealed that, in addition to the expected sea salt, combustion nuclei and soil particles were present. The latter were in the large particle range and were generally insoluble in water. Since these measurements were made on cloud droplets, the particles found therein are likely to have been true condensation nuclei. Thus, it seems that even sea fog is caused by the presence in the atmosphere of particles of continental (and often probably of anthropogenic) origin.

Direct sampling with cascade impactors of various atmospheres followed by microchemical analyses for NH_4^+ , Na^+ , Mg^{++} , $\text{SO}_4^{=}$, Cl^- , NO_3^- , and NO_2^- analyses have shown:

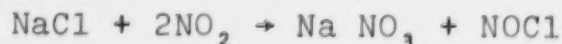
1. The inorganic composition of large particles consists primarily of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)\text{HSO}_4$. (The latter is ammonium bisulfate.) No NO_2^- was found and very minor amounts of Na^+ , Cl^- , and NO_3^- were found. This was so for inland and coastal regions.

2. Giant particles ($r > 1\mu$) generally showed the presence of sea salt, even for Central Europe. In addition to Na^+ and Cl^- , significant amounts of $\text{SO}_4^{=}$ and NO_3^- and small amounts of NH_4^+ were found.
3. There are systematic variations in concentrations of the various components of the two size categories of particles in proceeding from continental to maritime air. These are shown in the two diagrams of Figs. 1 and 2.

The Figures show that for large particles the concentrations of $\text{SO}_4^{=}$, NH_4^+ , NO_3^- , and Cl^- generally increase with distance inland. The Cl^- concentrations show a minimum a short distance inland because sea salt contributes some Cl^- to the large particles. This contribution decreases with distance inland until continental sources of Cl^- begin to affect the composition.

The giant particles exhibit interesting alterations in composition with distance inland. As in the case of large particles, NH_4^+ increases. This time, $\text{SO}_4^{=}$ has a minimum a short distance inland for reasons similar to that for Cl^- in large particles; Cl^- decreases with distance inland while NO_3^- increases with distance.

Junge interprets the behavior of Cl^- and NO_3^- in large particles as resulting from the reaction of NO_2 of continental origin with NaCl . This system, studied by Robbins, Cadle, and Eckhardt [264], consists of the series of reactions:



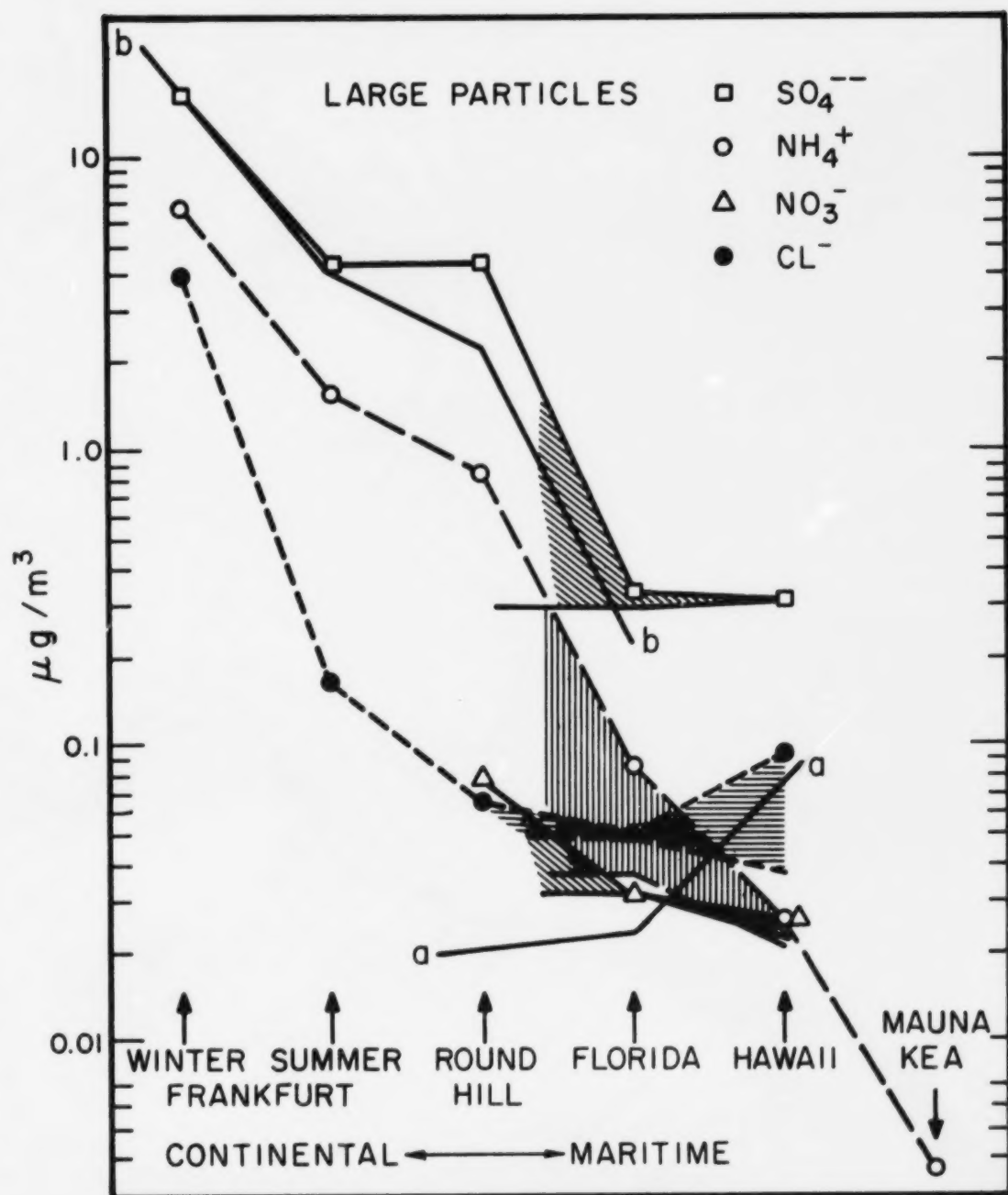


FIG.1 SURVEY OF THE AVERAGE CHEMICAL COMPOSITION OF LARGE PARTICLES. THE VARIOUS SITES ARE ARRANGED WITH RESPECT TO THEIR CONTINENTAL AND MARITIME CHARACTER. THE SHADED AREAS INDICATE THE DIFFERENCE BETWEEN THE ACTUAL VALUES AND THE CORRESPONDING LIMITS OF DETECTION.

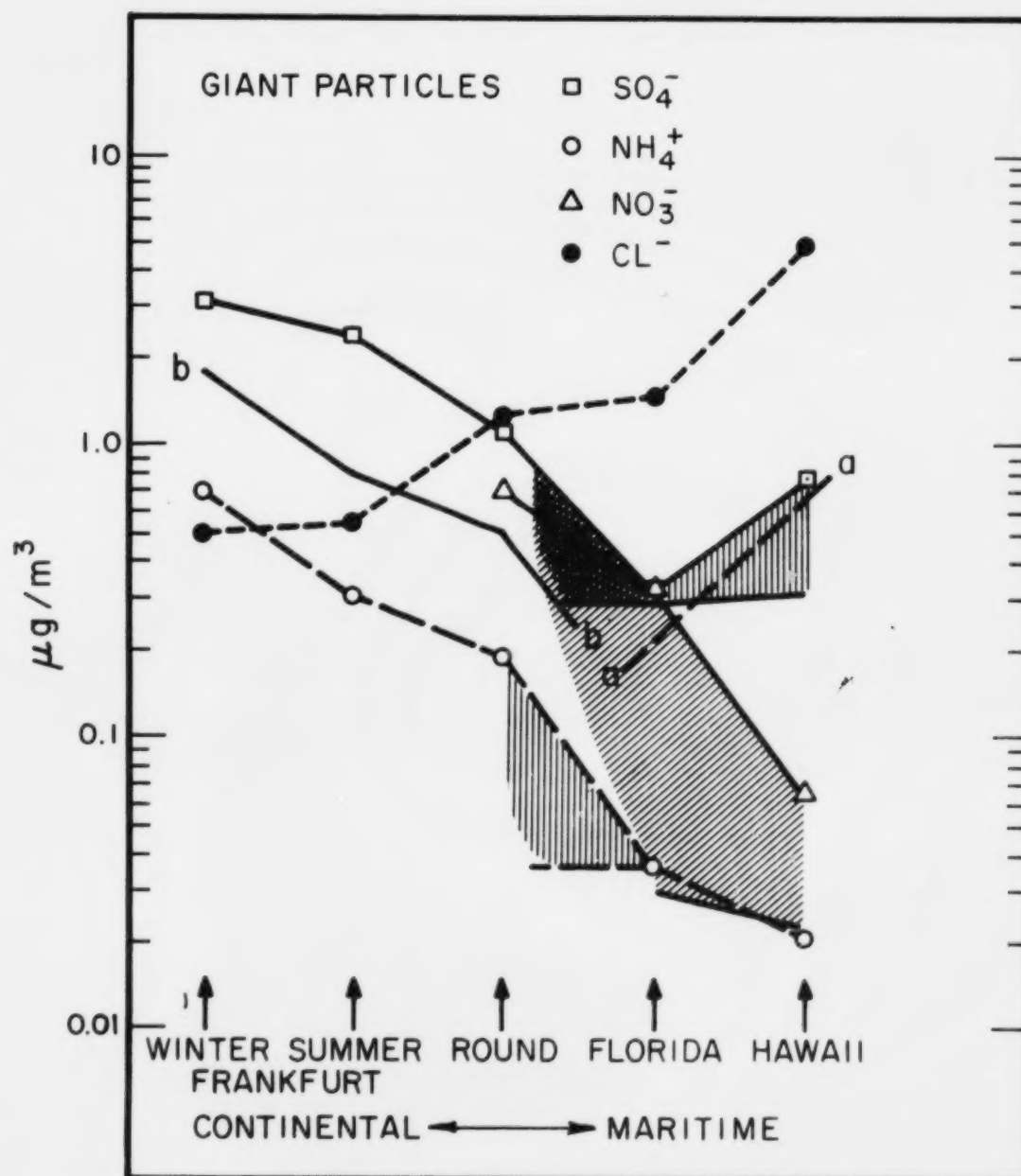


FIG.2 THE SAME AS FIG.1, BUT FOR GIANT PARTICLES.

The reactions proceed slowly but completely at room temperature. Since no NO_2^- was found in the samples, it is reasonable to suppose that HNO_2 becomes readily oxidized in the atmosphere to HNO_3 .

The explanation for the ubiquitous presence of ammonium sulfate in large particles is that SO_2 is oxidized by one or more mechanisms to form sulfate. The details of the probable mechanisms will be discussed under Sec. III-B, "Transformation of Sulfur Compounds in the Atmosphere."

In addition to the Japanese studies of cloud and fog water mentioned earlier, studies by Oddie [228] and Petrenchuk and Drozdova [237] have shown principal inorganic components of $\text{SO}_4^{=}$, NO_3^- , Cl^- , NH_4^+ , and Ca^{++} with smaller amounts of Mg^{++} , Na^+ , and K^+ . Clouds and fogs over maritime regions generally have compositions similar to sea salt except for the deficit of Cl^- , as noted before. Larger excesses of $\text{SO}_4^{=}$, NH_4^+ , and Ca^{++} relative to Cl^- are characteristic of clouds over polluted regions.

Thus far, attention has been focused on inorganic constituents of aerosols. The figures in Table I (obtained by Chambers *et al.* [38] from analyses of particles in nonurban atmospheres) clearly show that the total mass is not nearly accounted for by the inorganic constituents and that even the amount of acetone soluble material is only on the order of 15%. The remainder is presumably insoluble organic and carbonaceous matter. Neumann *et al.* [227] made a careful set of analyses of organic carbon in precipitation over Sweden and found that the ratio of carbon to inorganic material ranged from 0.28 to 1.03.

Went [372,373] found quantities of about 3% -7% of organic material in solids from Greenland and arctic ice island snows. These observations point up the importance of organic material in natural aerosols.

TABLE I. Particulate analyses in $\mu\text{g}/\text{m}^3$ from nonurban areas.^a

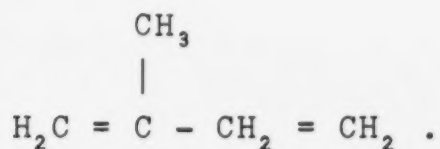
	Boonsboro	Salt Lake City	Atlanta	Cincinnati	Portland (Oregon)
Total load	68.0	55.0	71.0	45.0	86.0
Acetone soluble	8.7	6.2	9.3	9.0	12.6
Fe	3.7	4.1	2.7	2.4	3.6
Pb	0.1	0.1	0.9	0.4	0.3
F ⁻	—	—	Nil	0.26	—
Mn	0.00	0.04	0.11	0.07	0.04
Cu	Nil	0.28	0.01	0.19	<0.01
V	0.003	Nil	0.004	<0.001	0.002
Ti	0.26	Nil	0.13	0.01	Nil
Sn	<0.01	<0.01	<0.01	0.01	<0.01
As	0.01	0.03	0.01	<0.01	0.04
Be	0.0001	<0.0001	0.0002	0.0001	0.0001
SO ₄ ⁼	0.3	<0.01	0.5	1.9	0.4
NO ₃ ⁻	—	—	—	0.7	—

^aChambers *et al.* [38].

The role of organic Aitken nuclei in producing optical extinction has been studied more by F.W. Went than any other person. Using a Rich CN recorder in one case [374] and a CN meter and gas chromatograph in other cases [254], Went uncovered remarkable information, summarized in his paper "On the nature of Aitken

condensation nuclei" [374]. The essential features of his findings are: (a) volatile hydrocarbon compounds, mostly in the terpene series, are emitted by vegetation, including trees, forbs, algae, and plankton; (b) the concentrations ranged from 2 to 20 parts per billions (ppb) in twelve U.S. locations, one in the Netherlands, and one in a Costa Rican rain forest; (c) the concentrations of terpenes are high in the autumn, intermediate in spring and summer, and low in winter; (d) high concentrations are associated with dying leaves and mown hay; (e) sunlight plus nitrogen dioxide (NO_2) in the presence of terpenes causes the formation of a blue haze; (f) this haze apparently is identical to the hazes so prevalent in rural areas such as the Smoky Mountains; and (g) the condensation nuclei so formed decrease in number during the night and also with height above the ground.

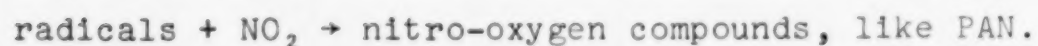
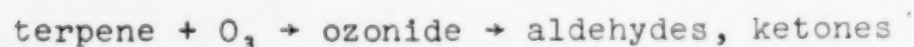
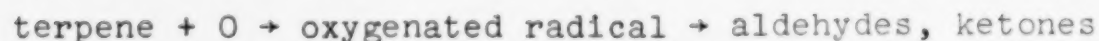
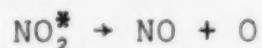
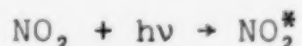
The remarkable fact is that the process of haze formation is analagous to the formation of photochemical smog from atmospheric mixtures containing olefins and NO_2 in sunlight. This subject will be treated later. However, for our present purposes, a simple listing of probable reactions will aid in fixing ideas. First, a short discussion of terpenes is in order. Terpenes are hydrocarbons having as basic structural units a five-carbon framework arranged as in the compound isoprene



Terpenoid compounds such as α -pinene and menthene contain double bonds which make them chemically similar to olefine compounds such as ethylene, propene, and butene, all having the structure



The significant reactions involving formation of the natural blue haze, if the reactions are similar to those producing photochemical smog in Los Angeles, are



Other reactions involving NO, NO₂, O, and a number of free radicals and short-lived species are usually considered to occur and probably do in this case; but the purpose of the list is to illustrate how the aerosol forms, not to account for chemical balances. The reactions produce high-molecular-weight, oxygenated organic molecules which have such low volatility that they cannot exist as single molecules in the atmosphere. In a stably stratified atmosphere with low wind speeds, collisions of these nonvolatile molecules with one another soon produces particles in the Aitken nuclei size range. From filter samples of cloud air over the Ozarks in summer, Went found concentrations of solid materials to be of the order of 0.1–0.3 mg m⁻³. From this, he estimates an average CN radius of 0.15 μ. This is nearly an order of magnitude larger than Junge's estimated radius of 0.025 μ for Aitken nuclei; but it is what is needed for producing the light scattering effect.

Went [374] estimates annual production of natural organic CN to be of the order of 10⁹ tons over the globe. This can be compared

to the total annual global emissions of sulfur in SO_2 and H_2S , both naturally and through combustion of fuels, of approximately 10^9 tons of SO_2 equivalent [151].

Suspended soil particles make up a portion of the natural continental aerosols which can limit visibility significantly during high winds. There have been few studies of the chemical nature of these suspended dust particles. In general, the particles are identifiable as mineral grains [138]. The smaller size grains become airborne most readily. The composition of the airborne particles depends upon the combined and interrelated effects of weathering and soil (or rock) type. Krumbein and Sloss [166] reported that studies of loess deposits in Illinois show an average particle radius of about 15μ for dust near the source. This average radius of the loess particles decreased to about 8μ at a distance of about 100 km from the source. Insofar as chemical composition and grain size may be related, the chemistry of airborne soil particles will vary with distance from the source(s) as well as with source type. Transport of soil particles over intercontinental distances has been detected both directly (by Glawion [104] and recently by Bricker and Prospero [26]) and in pelagic sediments [262]. The number concentrations of soil particles involved in long-range transport is so small as to be insignificant with respect to obscured visibility.

Clouds from volcanic eruptions cause visibility restrictions generally of a localized and transient nature. The primary particulate emissions consist of lava ashes and other inorganic materials (of which ammonium sulfate has been identified [34]). Optical effects such as Bishop's rings (observed after Krakatao) and twilight scattering (the purple light and the golden glow)

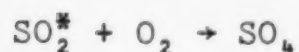
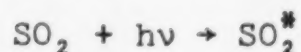
have been observed following notable eruptions. The eruption of Mt. Agung in Bali in March 1963 afforded an opportunity for study of global scale optical effects [361,211,66,112]. The global scale effects are caused by enhancement of particle concentrations in the lower stratosphere. While these effects are measurable, they do not constitute a significant visibility restriction. There exists little direct evidence of the chemical composition of the "volcanic dust" in the stratosphere. It seems likely that it is ammonium sulfate and/or sulfuric acid created by oxidation of SO_2 from the volcanic emissions. As such, the "volcanic dust" then constitutes an enhancement to the already present stratospheric aerosol of ammonium sulfate [87].

B. Transformation of Sulfur Compounds in the Atmosphere

This topic is interposed between the main divisions of the Chapter because it represents a bridge, or a common relationship between natural aerosols and urban pollution aerosols. As has been seen, ammonium sulfate occurs in almost all natural aerosols in the stratosphere as well as the troposphere and even in those of volcanic origin. There is probably not an urban region in the world in which the sulfate content of the suspended particulate is small compared to other inorganic species. The abiding question is: What are the origins of sulfate in natural and pollution aerosols? The most generally acceptable single answer is: Through the oxidation of SO_2 . This however is not very enlightening in terms of mechanisms. Three chemical systems thought to be pertinent to the problem have been studied.

(1) *Photo-oxidation of SO₂:*

The system of SO₂ in humidified air irradiated with ultraviolet high (artificial sunlight) and natural sunlight was studied by Gerhard and Johnstone [99]. They analyzed samples of sulfuric acid aerosol from the test chamber to determine the extent of reaction at various times. The reaction rate was judged to be first order with respect to SO₂ and Gerhard and Johnstone proposed that this was consistent with the mechanism:



The rate of conversion of SO₂ was estimated to be 0.1% per hour in natural noontime sunlight. Studies using special filters indicated that the effective solar radiation was in the wavelength region between 3000 and 3200 Å.

Judging from the published graphs of concentrations of H₂SO₄ versus time for various concentrations of SO₂, there was a fairly large spread in points for the run with 20 ppm of SO₂ - the run for which most replication was performed. Also, only three observation times were used for most experiments, with others having one or two times.

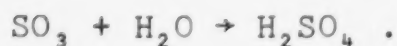
It is of interest to note that Urone *et al.* [351] irradiated a reaction flask containing SO₂ (12 ppm) in air with 50% relative humidity with artificial UV-light for 30 hr and obtained a conversion rate of 0.1% per hour of equivalent noontime sunlight, thus apparently verifying the results of Gerhard and Johnstone. Urone *et al.*, however, found that, in the presence of NaCl aerosol, the

rate of conversion of SO_2 in UV light was a factor of 13 higher than in the absence of aerosol. Gerhard and Johnstone, on the other hand, reported finding "no effect of nucleation on the amount of aerosol product" after making several runs with NaCl aerosol added to the airstream entering the reaction chamber.

The reason for the differences between the two experiments is not clear. It does seem clear, however, from the results of Urone *et al.* that the conversion of SO_2 by UV, at least in this experiment, was not entirely by homogeneous gas phase reactions. Perhaps the agreement of the SO_2 -air-UV experiments was real (if the vessel wall was not as effective as NaCl) or perhaps it was fortuitous. Further investigations of this system would be warranted. Urone *et al.* found significant conversions of SO_2 in the dark in the presence of aerosols of Fe_2O_3 , Cr_2O_3 , PbO , PbO_2 , CaO , and mixtures of CaO and Al_2O_3 . The most notable dark conversion rate was found using dried Fe_2O_3 aerosol. The reaction was complete within seconds of introduction of the air- SO_2 mixture into the flask.

(2) *Reaction of SO_2 with Atomic Oxygen:*

Cadle and Powers [35] studied the kinetics of conversion of SO_2 to sulfuric acid via the mechanism



The second reaction is thought to be extremely fast so that rate studies using the disappearance of SO_2 and O would yield proper information for the high reaction. The result of Cadle and Powers consisted of a measurement of the third-order reaction rate constant k in:

$$-\frac{d(\text{SO}_2)}{dt} = -\frac{d(\text{O})}{dt} = k(\text{SO}_2)(\text{O})(\text{M}) .$$

The value obtained was $1.3 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$ and it was relatively independent of temperature. The rate constant was the same for $\text{M}=\text{N}_2$ and $\text{M}=\text{O}_2$.

(3) *Catalytic oxidation of SO_2 in solution:*

Nearly concurrent studies of systems of SO_2 in solutions containing dissolved catalysts were conducted by Junge and Ryan [152] and by Johnstone and Coughanowr [150]. The latter study was of the kinetics of the absorption of SO_2 by drops and bulk quantities by solution. Junge and Ryan primarily studied the initial and final states of SO_2 solution systems.

Johnstone and Coughanowr found that solutions of MnSO_4 in the concentration range $4-15 \mu\text{g-cm}^{-3}$ absorbed SO_2 and produced $\text{SO}_4^{=}$ in solution. The initial rates of reaction were larger with no H_2SO_4 initially present than they were with initial concentrations of 0.002M H_2SO_4 and larger. It was also found that MnSO_4 and the mixtures $\text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3$ and $\text{MnSO}_4 + \text{CaSO}_4$ were effective catalysts at concentrations of $500 \mu\text{g-cm}^{-3}$ whereas FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and NiSO_4 were not nearly as effective even at concentrations of the order of $1000 \mu\text{g-cm}^{-3}$ or more. Johnstone and Coughanowr interpreted their experimental results as consistent with the theory that, for dilute MnSO_4 solutions in drop form, the reaction whereby SO_2 is converted to $\text{SO}_4^{=}$ occurs throughout the volume of the drop. They estimated that, in a fog with 1 ppm of SO_2 , the oxidation rate of SO_2 would be about 1% per minute - a factor of about 500 times the photochemical conversion rate found by Gerhard and Johnstone [99] for noonday sun.

Junge and Ryan, in one part of their experiment, studied the rate of conversion of SO_2 to $\text{SO}_4^{=}$ in solutions of $1\mu\text{g-cm}^{-3}\text{FeCl}_3$. They found that within a period of three hours all reaction had ceased for SO_2 concentrations in air of 1.5×10^4 and $4.2 \times 10^4 \mu\text{g-m}^{-3}$. (For SO_2 $1\mu\text{g-m}^{-3} = 3.5 \times 10^{-4}\text{ppm}$.) The slopes of their time - $\text{SO}_4^{=}$ curves give initial values of 0.0006 and 0.018 mmole $^{-1} \text{-min}^{-1}$, respectively, which are to be compared to Johnstone and Coughanowr's zeroth order rate constant of 0.026 mmole $^{-1} \text{-min}^{-1}$ for a system using SO_2 dissolved in water and mixing with a solution of $4\mu\text{g-cm}^{-3}\text{MnSO}_4$. In this circumstance, the SO_2 equilibrium vapor pressure for the solution would have been of the order of 1 atmosphere, or about a factor of 10^5 higher than in the experiment of Junge and Ryan. In this respect the two different experiments are not comparable and therein probably lies the explanation for the apparent good catalysis by FeCl_3 for Junge and Ryan and the relatively poor catalysis by $\text{Fe}_2(\text{SO}_4)_3$ for Johnstone and Coughanowr. Junge and Ryan found larger conversions after three hours of exposure for solutions of $1\mu\text{g-cm}^{-3}$ of MnCl_2 and CoCl_2 than for FeCl_3 - the three final concentrations being 329, 199, and $167 \mu\text{g-cm}^{-3}$, respectively. For NH_4OH and CoCl_2 , they found lower conversions of $49\mu\text{g-cm}^{-3}$ and much lower amounts for NaCl and distilled water (4 and $3 \mu\text{g-cm}^{-3}$, respectively).

Junge and Ryan also found that the pH of the solution drastically altered the amount of sulfate formed in the pH range of 5 to about 2.2. For pH values of 5 or greater, there is no effect and the conversion is high. For pH values below 2.2, the conversion is very low. The concentrations of $\text{SO}_4^{=}$ in $1\mu\text{g-cm}^{-3}\text{FeCl}_3$ solutions corresponding to the extreme pH values are $150\mu\text{g-cm}^{-3}$ and about $5 - 10\mu\text{g-cm}^{-3}$.

Junge and Ryan studied also the system SO_2 - NH_3 - liquid H_2O using solutions through which SO_2 and NH_3 gases were bubbled and

also using droplets nucleated by NaCl aerosol and exposed to SO_2 and NH_3 gases. The results were that much greater conversions of SO_2 to $\text{SO}_4^{=}$ were achieved because NH_3 serves not only to provide catalyst NH_4^+ but also to neutralize the sulfuric acid formed to keep the pH well above the 2.2 level, below which little conversion could occur. Limiting amounts of conversion were apparently observed in the droplet experiment; i.e., it was observed that after 15 minutes of exposure no further NH_4^+ was produced, implying that no more oxidation of SO_2 was occurring. Junge and Ryan, using equilibrium considerations and assuming that the final concentration of $\text{SO}_4^{=}$ in solution is proportional to the SO_2 contents of the air, showed that the chemical system studied can essentially explain the concentrations of NH_4^+ and $\text{SO}_4^{=}$ observed in fog water from both polluted and unpolluted atmosphere. To make the calculations they used some typical observed values of SO_2 in these atmospheres but they had to assume the NH_3 concentration in polluted atmospheres.

Scott and Hobbs [286] performed a theoretical study of the SO_2 - NH_3 -liquid H_2O -air system in which they considered all of the equilibria involved (including $\text{H}_2\text{O} + \text{CO}_2 = \text{H}^+ + \text{HCO}_3^-$) and assumed that the rate determining step is oxidation of $\text{SO}_3^{=}$ to $\text{SO}_4^{=}$ and that

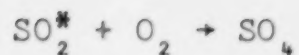
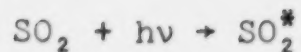
$$\frac{d(\text{SO}_4^{=})}{dt} = k(\text{SO}_3^{=}) .$$

This was probably a more chemically correct system with regard to the equilibria studied. The assumption of the rate determining step seems reasonable since the equilibria are generally rapidly attained. It was thus not necessary to use the limiting conversion concept. Scott and Hobbs found that the amount of conversion was not limited; so the $\text{SO}_4^{=}$ concentration continues to increase with slowly decreasing rate with time. These results in no way obviate Junge and Ryan's conclusions concerning the possible

importance of this system in explaining the presence in fogs and clouds of ammonium sulfate.

In reviewing the occurrences of natural ammonium sulfate in light of the foregoing three mechanisms, the following conclusions can be drawn:

1. Catalytic oxidation of SO_2 in solution to form ammonium sulfate probably accounts for its presence in fog and cloud drops in nonurban air. There is always a larger mass concentration of SO_2 gas than of equivalent SO_2 in aerosol, even in "clean" air [151]. Also implied in this explanation is the presence of NH_3 gas. Junge [151] gives clean air concentrations of the order of $1-10 \mu\text{g-m}^{-3}$ of NH_3 , with an average of about $3\gamma\text{-m}^{-3}$. This is in excess of the average NH_4^+ contents of fog water (which would amount to a concentration in the atmosphere of about $1\mu\text{g-m}^{-3}$) [152]. Thus, it seems that the autocatalytic effect of the SO_2 - NH_3 -liquid H_2O system, coupled with its ability to maintain a high pH in solution, accounts for the presence of natural ammonium sulfate in clouds and fog. The presence of $(\text{NH}_4)_2\text{SO}_4$ in dry aerosol in rural air might, to a great extent, be accounted for by the same mechanism followed by evaporation of the water thus leaving only the solid material behind [152]. These particles in turn may become condensation nuclei for cloud drops.
2. The photoexcitation mechanism of Gerhard and Johnstone, if it occurs, cannot account for a significant amount of conversion of natural SO_2 to sulfate because the residence time of SO_2 in the global cycle is of the order of about seven days [151], and the half-life of SO_2 with respect to the first-order oxidation of SO_2 via



is of the order of 30 days. The atmospheric residence half-time would be longer because of its dependency on sunlight.

It was shown by Prager, Stevens, and Scott [246] that SO_2 does not react with O_3 in the dark. This rules out the possibility that the reaction



contributes to the production of sulfate in the atmosphere.

C. Haze Formation in Urban Atmosphere

Any urban atmosphere characteristically contains very large concentrations of Aiken nuclei and large particles, compared to rural or maritime regions. These particles may of themselves account for visibility limitations or they may enhance the formation of fogs and clouds that further obscure visibility.

Detailed chemical knowledge that can directly relate to visibility is fragmentary in general. And indeed the emissions of particles and their subsequent alteration in the atmosphere exhibit time and space patterns that are highly individualistic for each urban region.

Two summary works give chemical information relating to aerosols and visibility in urban atmosphere. The first, a chapter by

Corn [45] in Stern's book *Air Pollution* [321] deals with "Nonviable Particles in the Atmosphere" and contains 141 references to work through 1966. The material pertinent to the chemical aspects of visibility is itemized below.

Urban sulfates. Since sulfate is always found in urban atmospheric particulate samples (see Tables II and III), it is interesting to determine the size distributions of the sulfate-bearing particles by means of cascade impactors or a Geotz aerosol spectrometer. In London, fog droplets are acidic, hence the terms "sulfuric acid aerosol" or "sulfuric acid droplet" have come into usage. This should not be confused with the aerosol which would result from the reaction of SO_3 and water vapor in a relatively dry atmosphere. The sulfuric acid in London fogs is probably created by the catalytic oxidation of SO_2 to $\text{SO}_4^=$ in solution as per Junge and Ryan. In samples of London air with high humidity (14 January 1959), Waller [367] found the mass median diameter of the sulfuric acid droplets to be about 0.5μ . At lower humidities this diameter was smaller. Table IV compiles some results of various limited sulfate size-distribution determinations.

The study of Los Angeles by Ludwig and Robinson [198], in addition to showing a variation in droplet size with humidity, showed complicated diurnal dependency and also some geographical differences.

In Los Angeles and San Francisco, the very small particles at low humidities may have been created by one or both of the photochemical mechanisms previously discussed, namely,

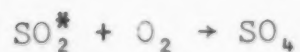


TABLE II. Mean and maximum concentrations of selected particulate contaminants in U.S. atmospheres^a 1957-1964.

Pollutant	Pollutant Concentration ($\mu\text{g}/\text{m}^3$)	
	Geo. mean	Max.
Suspended particulates	98.	1706.
Benzene-soluble organics	7.4 ^b	128.3
Nitrates	1.68	24.8
Sulfates	9.35	95.3
Antimony	<i>c</i>	—
Bismuth	<i>c</i>	—
Cadmium	<i>c</i>	—
Chromium	0.020	0.710
Cobalt	<i>c</i>	—
Copper	0.063	10.00
Iron	1.99	74.00
Lead	0.54	17.00
Manganese	0.064	4.70
Molybdenum	<i>c</i>	—
Nickel	0.028	0.830
Tin	0.024	1.00
Titanium	0.042	1.14
Vanadium	<i>c</i>	—
Zinc	0.09	58.00
Radioactivity (in $\mu\text{c}/\text{m}^3$)	4.7 ^d	5435.00

^aBased on samples collected during a 24-hour period.

^b1957-1963 Mean, 1964 samples have been composited by quarters.

^cConcentrations in most samples are below minimum detectable quantity.

^dArithmetic average of national monthly averages.

TABLE III. Particulate analyses from selected urban locations: arithmetic mean values for 1964 expressed as micrograms per cubic meter.^a

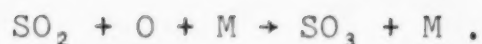
	Atlanta	Chicago	Boston	Pittsburgh
Suspended particulates	97	176	144	174
Benzene-soluble organics	7.6	9.5	9.1	10.0
Sulfates	4.8	19.0	18.1	17.5
Nitrates	2.0	2.5	2.3	3.0
Chromium	<i>b</i>	0.014	0.007	0.021
Cadmium	<i>b</i>	<i>c</i>	<i>c</i>	<i>c</i>
Iron	<i>b</i>	1.6	0.9	2.8
Lead	<i>b</i>	0.9	0.9	0.9
Manganese	<i>b</i>	0.07	0.03	0.21
Nickel	<i>b</i>	0.042	0.76	0.026
Tin	<i>b</i>	0.02	0.01	0.01
Titanium	<i>b</i>	0.02	0.02	0.05
Zinc	<i>b</i>	0.95	0.33	1.06

^aSource: National Air Sampling Network Data.^bNot analyzed.^cMost samples are below minimum detectable quantity.

TABLE IV. Mass median diameters of sulfate aerosols.

Location	No. of Samples	Mass Median Diameter (μ)	Rel. Humidity (%)	Investigators
Pittsburgh	27	2.6	17 - 90	Corn and DeMalo, 1965
Cincinnati	7	0.45	—	Roesler <i>et al.</i> , 1965
	24	0.42	>40	Wagman <i>et al.</i> , 1967
Chicago	7	0.32	—	Roesler <i>et al.</i> , 1965
	24	0.42	>40	Wagman <i>et al.</i> , 1967
Los Angeles and San Francisco	4	0.11	12.5 - 27.5	Ludwig & Robinson, 1968
	4	0.35	27.5 - 42.5	Ludwig & Robinson, 1968
	16	0.30	42.5 - 57.5	Ludwig & Robinson, 1968
	33	0.62	57.5 - 72.5	Ludwig & Robinson, 1968
	10	1.1	72.5 - 87.5	Ludwig & Robinson, 1968
Philadelphia	24	0.66	>40	Wagman <i>et al.</i> , 1967
Fairfax, Ohio	24	0.66	>40	Wagman <i>et al.</i> , 1967

and



Another more likely explanation is discussed further in this Chapter.

Trace metals. Recently the size distributions of trace metals have been determined by sampling techniques similar to those used for sulfate. Table V shows size distributions and concentrations of lead-bearing aerosols in downtown Los Angeles as determined by Robinson *et al.* [267]. The principle source of particulate lead in urban (and perhaps all nonindustrial) atmospheres is believed to be the combustion of gasoline containing lead alkyl compounds as antiknock additives. Table VI shows the results of a recent study performed by Lee, Patterson, and Wagman [181] of the size distributions of trace metals in urban aerosols. (Fairfax is a suburb of Cincinnati.)

The results of these studies show that the trace metals are a relatively small fraction of the mass of suspended particulate. They may, singly or in concert, act as catalysts for the solution oxidation of SO_2 , and, in this way, play a role in visibility restriction, as has previously been indicated for sulfate large particles.

Another possible manner in which a trace metal, namely lead, could affect visibility was suggested by Schaefer [278]. He suggested that lead in particles could react with atmospheric iodine to form ice nuclei. Schaefer observed that particles collected under inversion conditions near cities reacted with iodine to form ice nuclei, thus leading him to the above suggestion.

TABLE V. Lead aerosol size-distribution tests: summary of downtown Los Angeles results.^a

Time	Size-Frequency Distribution (μ)						Average Concentration ($\mu\text{g}/\text{m}^3$)
	25%	40%	MMD ^b	60%	75%	90%	
A.M. and P.M.	0.096	0.12	0.14	0.17	0.55	—	3.37
A.M. and P.M.	0.11	0.15	0.15	0.23	0.42	—	4.31
A.M. and P.M.	0.11	0.16	0.16	0.26	0.40	—	5.53
A.M.	—	0.19	0.19	0.30	0.55	—	4.23
P.M.	—	0.19	0.19	0.29	0.50	—	3.75
A.M.	—	—	—	0.45	0.90	1.6	10.1
P.M.	—	0.21	0.21	0.32	0.46	—	7.61
A.M.	0.075	0.13	0.13	0.23	0.35	—	9.05
P.M.	—	—	—	0.20	0.30	—	2.91
A.M. and P.M.	0.045	0.11	0.11	0.21	0.33	—	5.00

^aFrom Robinson *et al.*^bMass median diameter.

TABLE VI. Average metal concentration and size distribution.

Metal	Cincinnati, Ohio (8-23 Sept. 1966)		Fairfax, Ohio (3-16 Feb. 1967)	
	Concentration ($\mu\text{g}-\text{m}^{-3}$)	MMD, μ	Concentration ($\text{mg}-\text{m}^{-3}$)	MMD, μ
Fe	3.12	3.7	1.15	1.4
Cd	0.08	3.1	0.02	10 (est.)
Mg	7.21	4.5	0.42	7.2 (est.)
Cr	0.31	1.5	0.28	1.9
Pb	2.78	0.18 (est.)	0.69	0.42 (est.)
Cu	0.19	1.2	0.04	Not determined
Total particulate	Not measured	Not measured	44.7	1.2
SO ₄	10.0	0.42 (est.)	7.2	0.42 (est.)

Along similar lines, Kumai [167], in electron microscopic studies of ice fog crystals, ice crystals, and supercooled fog droplets from Fairbanks, Alaska, identified residues from sublimation or evaporation as particles formed in combustion of coal, fuel oil, and gasoline. Inorganic and organic particles could be distinguished, as could hygroscopic nuclei.

Organic aerosols and photochemical chains. Comparing the "suspended particulates" (i.e., the mass concentration of particles) with the sum of all of the inorganic materials in Table III can show that a large proportion of urban atmospheric particulate material is organic. The difference in the above quantities plus the benzene-soluble organics is indicative of the magnitude of organic and carbonaceous material present. SiO_2 , Al_2O_3 , and Ca-compounds will certainly make up a small portion of the difference, since these materials are mostly found in dustfall rather than in suspended particulates. Table VII shows the results of analyses of polycyclic hydrocarbons from the benzene soluble portions of suspended particulate for various cities in the U.S. [277]. The chemical composition of the remainder of the organic particulate matter is relatively unknown. Table VIII from Sawicki *et al.* [277] shows a list of high molecular weight compounds and the concentrations relative both to the total particulate and to the atmosphere. This gives an idea of the complicated nature of the organic material to be expected in particles.

The second review paper from which material pertinent to visibility may be obtained is that by Altshuller and Buffalini [5] entitled "Photochemical Aspects of Air Pollution: A Review." Of special interest to the present topic is the section on aerosols. Much work has been performed in the general area of photochemical smog - Altshuller and Buffalini have 108 references. A summary of

TABLE VII. Polycyclic hydrocarbon content of suspended particulate matter for selected cities.^a

City	Month	Bghip ^b	BaP	BeP	BkF	P	Cor	Per	Anth	Total
Atlanta	Feb. 1959	8.9	7.4	4.7	6.0	6.0	4.3	1.1	0.52	38.93
Birmingham	Feb. 1959	18.	25.	10.	13.	17.	3.5	5.5	2.2	94.2
Detroit	Feb. 1959	33.	31.	23.	20.	25.	6.4	6.0	2.0	146.4
Los Angeles	Feb. 1959	18.	5.3	8.1	5.7	6.0	12.	1.6	0.16	56.86
Nashville	Jan. 1959	17.	25.	14.	15.	30.	4.6	4.4	1.8	111.8
New Orleans	Feb. 1959	7.3	4.1	6.4	3.9	2.3	27.	0.8	0.10	27.6
San Francisco	Jan. 1959	7.5	2.3	2.9	1.7	1.9	4.9	0.34	0.10	21.64
Atlanta	July 1958	5.1	1.6	1.5	1.3	0.73	2.5	0.40	0.2	13.3
Birmingham	July 1958	8.3	6.4	5.9	4.6	2.1	2.4	2.1	0.25	32.05
Detroit	July 1958	9.5	6.0	5.3	4.9	2.8	1.8	1.7	0.38	32.38
Los Angeles	July 1958	2.3	0.5	0.63	0.45	0.27	2.2	0.034	0.03	6.41
Nashville	July 1958	3.4	1.4	1.2	1.0	0.58	1.3	0.21	0.06	9.15
New Orleans	July 1958	4.6	2.0	3.1	1.8	0.34	2.5	0.39	0.1	14.8
San Francisco	July 1958	2.6	0.25	0.54	0.24	0.09	1.6	0.043	0.022	5.39

^aFrom Sawicki et al.^bBghip=benzo(g,h,i)perylene; BaP=benzo(a)pyrene; BeP=benzo(e)pyrene; BkF=benzo(k)fluoranthene; P=pyrene; Cor=coronene; Per=perylene; Anth=anthanthrene. Values in micrograms per 1000 m³.

TABLE VIII. Concentrations of large organic compounds in the average American urban atmosphere.^a

Compound	Airborne Particulate ($\mu\text{g}/\text{gm}$)	μg
		1000 m ³ air
Benzo(<i>f</i>)quinoline	2.	0.2
Benzo(<i>h</i>)quinoline	3.	0.3
Benzo(<i>a</i>)acridine	2.	0.2
Benzo(<i>c</i>)acridine	4.	0.6
11 H-Indeno(1,2- <i>b</i>)quinoline	1.	0.1
Dibenz(<i>a,h</i>)acridine	0.6	0.08
Dibenz(<i>a,j</i>)acridine	0.3	0.04
Benz(<i>a</i>)anthracene	~30.	~4.
Fluoranthene	~30.	~4.
Pyrene	42.	5.
Benzo(<i>a</i>)pyrene	46.	5.7
Benzo(<i>e</i>)pyrene	42.	5.
Perylene	5.5	0.7
Benzo(<i>ghi</i>)perylene	63.	8.
Anthanthrene	2.3	0.26
Coronene	15.	2.
<i>n</i> -Heptadecane	20.	2.5
<i>n</i> -Octadecane	110.	14.
<i>n</i> -Nonadecane	160.	20.

TABLE VIII (continued)

Compound	Airborne Particulate ($\mu\text{g}/\text{gm}$)	μg
		1000 m^3 air
<i>n</i> -Eicosane	180.	23.
<i>n</i> -Heneicosane	320.	40.
<i>n</i> -Docosane	480.	60.
<i>n</i> -Tricosane	620.	77.
<i>n</i> -Tetracosane	480.	60.
<i>n</i> -Tentacosane	480.	60.
<i>n</i> -Hexacosane	85.	11.
<i>n</i> -Heptacosane	260.	32.
<i>n</i> -Octacosane	340.	43.
Total	3800.	480.

^aFrom Sawicki *et al.* [277].

the material is given below without detailed references for the works cited by Altshuller and Buffalini.

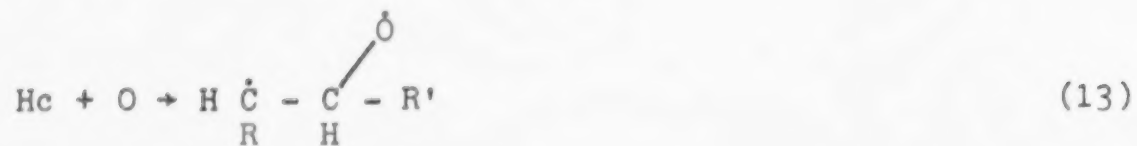
The list of the reactions thought to be significant in photo-chemical smog is given below:

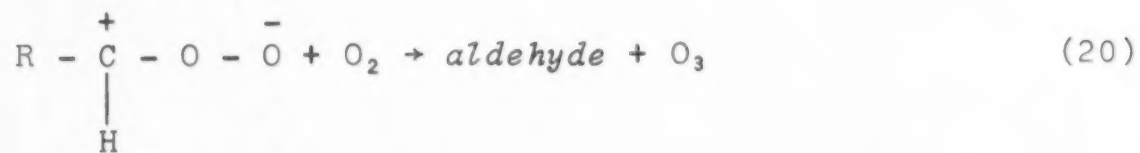
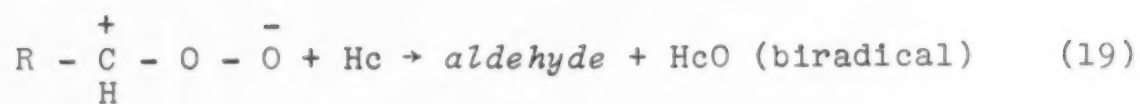
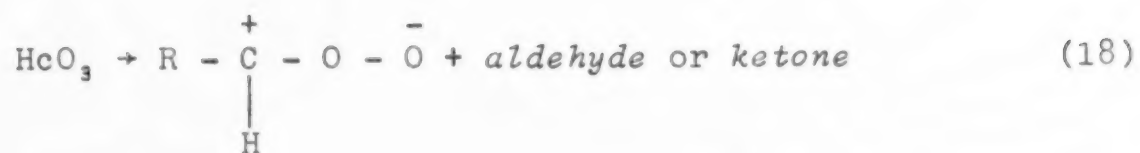
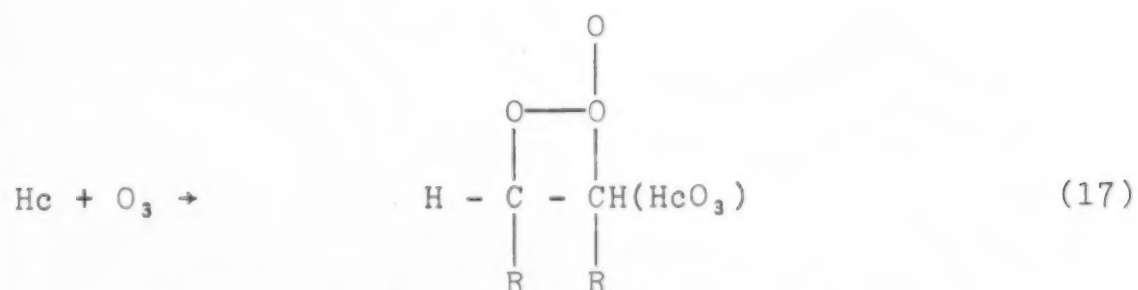
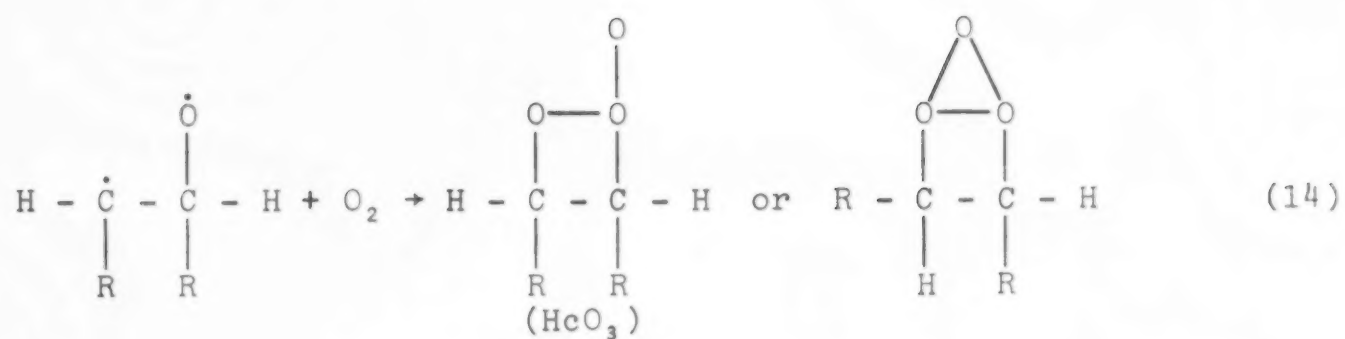


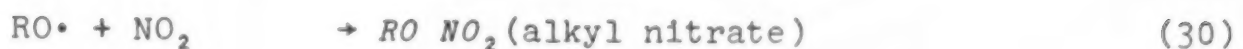
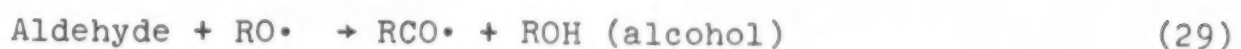


Hc = olefin or aromatic hydrocarbon

R, R' = alkyl fragment







It is important to note that reaction (1) is the principal source of O-atoms in polluted atmospheres (as it may also be in rural atmospheres where terpenes become involved in aerosol formation). Reactions (2), (20), and (26) account for the formation of ozone.

One of the prolonged mysteries of photochemical smog formation is the means by which NO becomes converted to NO₂ in the atmosphere. The reactions (5)–(8) in the list of important reactions serve to decrease the quantum yield of NO₂ photolysis [reaction (1)], but do not account for the net conversion of NO to NO₂.

Laboratory studies have shown that aerosol formation occurs in irradiated mixtures of olefins and NO₂ in air, both with and

without SO_2 present. This system was studied quite exhaustively by Goetz and Pueschel [106], who found that, for a variety of humidity conditions, aerosol formation as a function of SO_2 concentration was at a minimum in the vicinity of 1-2 ppm SO_2 . The aerosol formed without SO_2 present was volatile, while that produced in the presence of SO_2 was not volatile even for low humidities. At high humidities, H_2SO_4 droplets were found to be produced. Goetz and Pueschel interpret their finding of nonvolatile aerosol at low humidities to indicate that the particles are not H_2SO_4 .

The results of Goetz and Pueschel are interesting because they are consistent with the studies of Prager *et al.* [246], who found that copious aerosol formation occurred in irradiated automotive engine exhausts when fuel with sulfur content was used - the aerosol formation being much less in sulfur-free fuel. The aerosol is formed rapidly before the exhaust plume is diluted to the point where SO_2 concentrations are about 1-2 ppm - the region of minimum aerosol formation. Schuck and Doyle [281] and Reckner *et al.* [260] found that aerosol formation in olefin- NO_2 - SO_2 systems increased with increasing olefin concentrations but leveled off when the olefin concentration became equal to that of NO_2 . Altshuller and Buffalini note that this is about the same regime in which PAN (peroxyacyl nitrite) and O_3 formation are greatest. Altshuller and Buffalini suggest that the intermediate products formed in the irradiation may assist in the production of H_2SO_4 nuclei. On the other hand, it may be that the SO_2 somehow promotes the formation of complex organic-oxygen compounds perhaps through some intermediate sulfur compounds. This seems reasonable if Goetz and Pueschel are correct that the aerosol formed at low humidities does not contain significant H_2SO_4 .

This explanation and the results of Goetz and Pueschel are corroborated by the findings of Ludwig and Robinson [197] that at

very low humidities the size of sulfur-bearing particles is of the order of 0.11μ and the particles certainly do not comprise a significant portion of the total aerosol mass, or light scattering cross-section.

In view of the rapidity of the reactions discussed above, it does not seem probable that the Gerhard and Johnstone [99] reaction or the reaction



contributes significantly to aerosol formation. However, assuming an O-atom concentration of 10^{-8} ppm [182], the rate of conversion of SO_2 by the above reaction is estimated at $0.04\% \text{ hr}^{-1}$. This is not very different from the $0.1\% \text{ hr}^{-1}$ rate of the Gerhard and Johnstone reaction.

There has currently been considerable interest in singlet molecular oxygen and its role in atmospheric chemical reactions. Pitts *et al.* [240] have published a review paper on the topic. This species of excited molecular oxygen may exist in two quantum states, $^1\Delta_g$ and $^1\Sigma_g^+$. It may be produced by direct absorption of solar radiation, by collisional excitation and by photolysis of ozone. Singlet molecular oxygen is quite reactive - producing peroxy compounds by direct addition to olefinic compounds. Thus, singlet oxygen may comprise a part of the oxidant in photochemical smog and thereby contribute to aerosol formation. The significance of the role of singlet oxygen in the inorganic NO_2 -NO- O_2 system is not yet clearly understood. There have been no direct measurements of singlet molecular oxygen in a polluted atmosphere.

The only gaseous urban pollutant that is ordinarily considered to produce optical extinction in the atmosphere is NO_2 . The brownish color of atmospheres polluted by photochemical smog has been attributed to the absorption of light in the blue-green region of the visible spectrum by NO_2 [182,131]. Robinson [266] has

shown that the presence of aerosol lessens the relative contribution of extinction by NO_2 absorption.

The chemical behavior of NO_2 in photochemical smog has been the subject of extensive investigation (Altshuller and Buffalini [5]). Reactions (1) through (10) [pages 33 and 34] show how NO_2 and NO become involved in a purely inorganic system to produce O_3 and O -atoms. Reactions (21) through (31) [pages 35 and 36] show how organic materials become involved with NO and NO_2 to produce complex organic molecules, such as PAN.

The source of NO_2 is primarily combustion and, in cities such as Los Angeles, especially combustion in automotive engines. The system of atmospheric inorganic reactions can be shown to come to a steady state in NO_2 after several hours [322] if the source remains constant. In practice this situation does not occur — as automotive traffic diminishes after the morning rush hour, the source diminishes and, ultimately, the NO_2 plus NO concentrations decrease through removal reactions and dilution by atmospheric motions (see Fig. 3). We would expect the aerosol content in photochemical smogs to follow a pattern similar to that shown for O_3 in Fig. 3. However, since the processes of smog formation depend on sunlight, there is generally a smaller peak in $\text{NO}_2 + \text{NO}$ and aerosol corresponding to evening rush hours during the summer. After sunset in Los Angeles, drainage winds often carry the polluted air westward over the Pacific Ocean with attendant decreases in the concentration of all pollutants.

The ultimate fate of NO_2 is probably oxidation to nitrate in solution



[118].

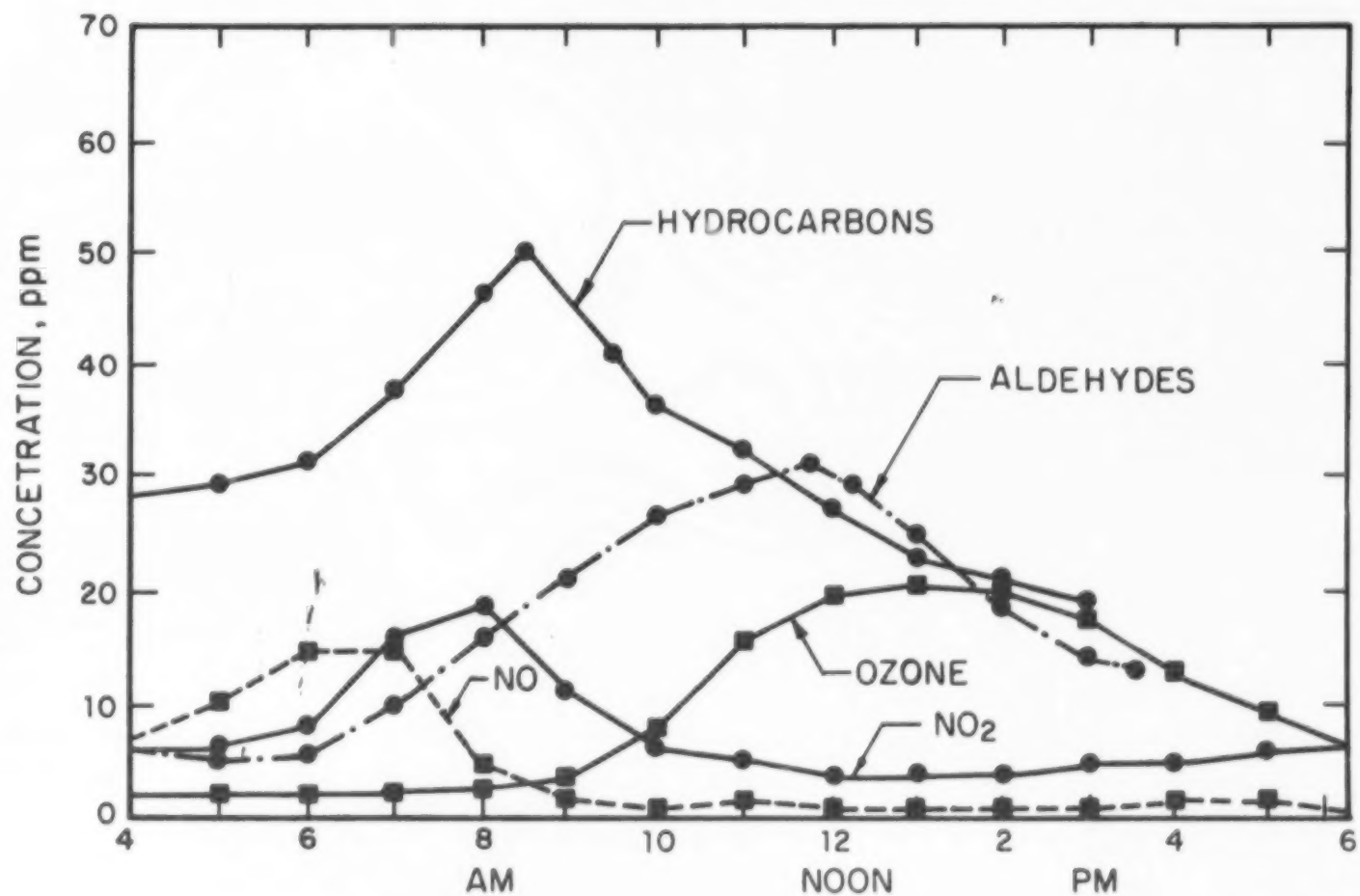
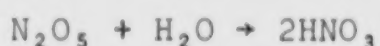


FIG.3 AVERAGE CONCENTRATIONS DURING DAYS OF EYE IRRITATION IN DOWNTOWN LOS ANGELES. HYDROCARBONS, ALDEHYDES, AND OZONE FOR 1953-1954. NITRIC ACID AND NITROGEN DIOXIDE FOR 1958. FROM DATA OF THE LOS ANGELES COUNTY AIR POLLUTION CONTROL DISTRICT.

In regions where O_3 concentrations are high, the reactions



may occur [118].

D. Humidity Effects and Classification System for the Optical State of the Atmosphere

One of the necessary steps in studying the formation of hazes appears to be the introduction of an appropriate classification system for the optical weather.* G.V. Rozenberg [271] suggested such a system based on the analysis of a complex of optical characteristics and introduced four basic types of the optical state of the atmosphere: haze, dense haze, fog, and drizzle [200,61,107,108,109,274]. Haze is usually associated with the visibility range of more than 3 km; dense haze corresponds to the visibility from 1 to 3 km; visibility during fog is less than 1 km.

These types of optical weather were shown to be related to certain ranges of relative humidity (see Fig. 4). The role of the latter in the processes leading to formation of hazes becomes more clear after the analysis of correlations between the relative humidity and other optical characteristics of aerosol.

Figure 5 shows the correlation between the scattering coefficient of the air volume for visible radiation and its relative humidity [97]. Examples of other correlations are presented in Fig. 6, which illustrates statistical dependence of the anisotropy of the scattering function and of the maximum ellipticity of the polarization of the scattered light on the relative humidity [109].

*The physical basis for such system, i.e., the studies of the optical properties of aerosols, is presented in detail in Chap. VI.

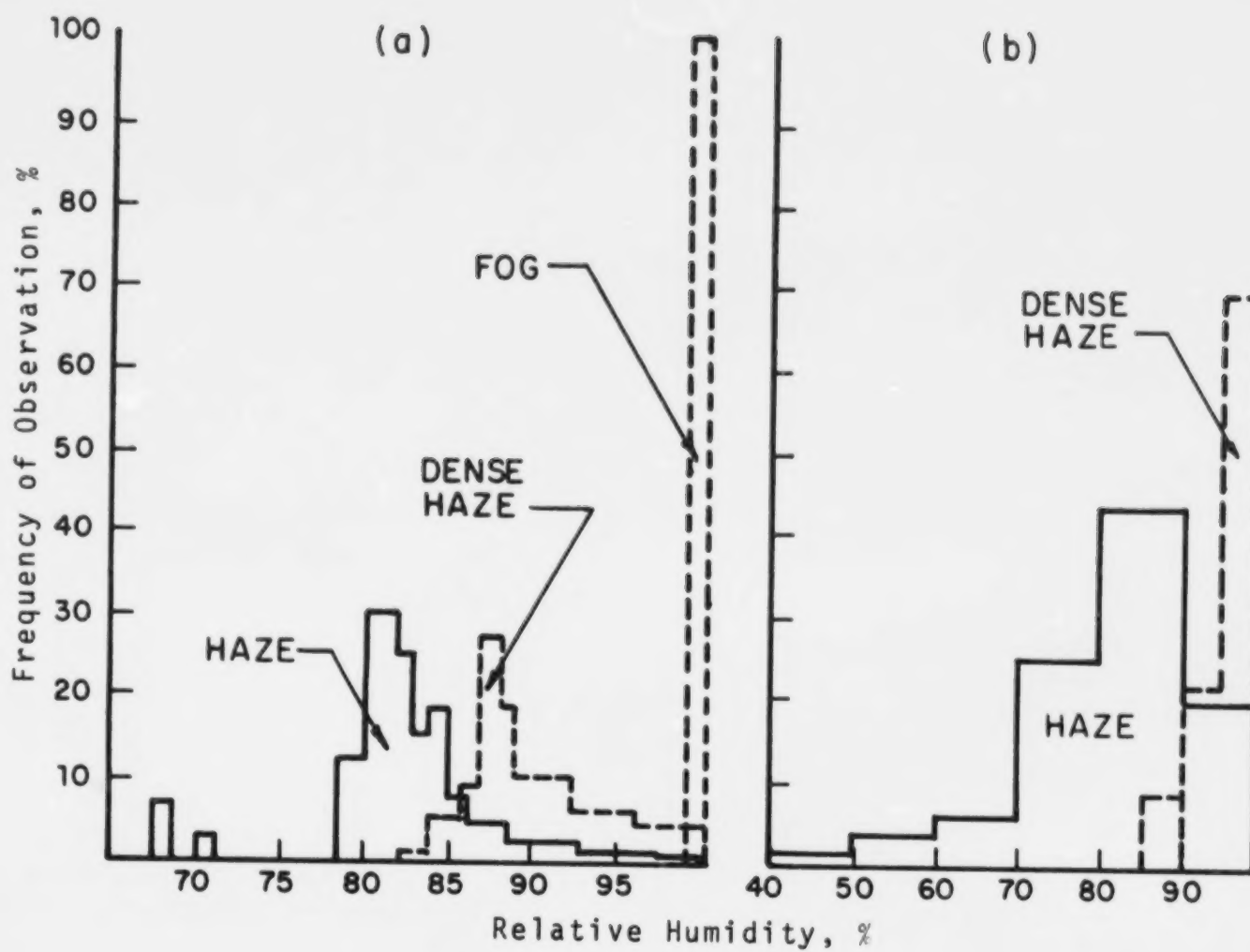


FIG.4 HISTOGRAMS SHOWING THE RELATIVE FREQUENCY OF OCCURRENCE OF HAZES AND DENSE HAZES, AS A FUNCTION OF RELATIVE HUMIDITY: (a) FROM AUREOLE MEASUREMENTS; (b) FROM THE ANGULAR DEPENDENCE OF THE SCATTERING MATRIX.

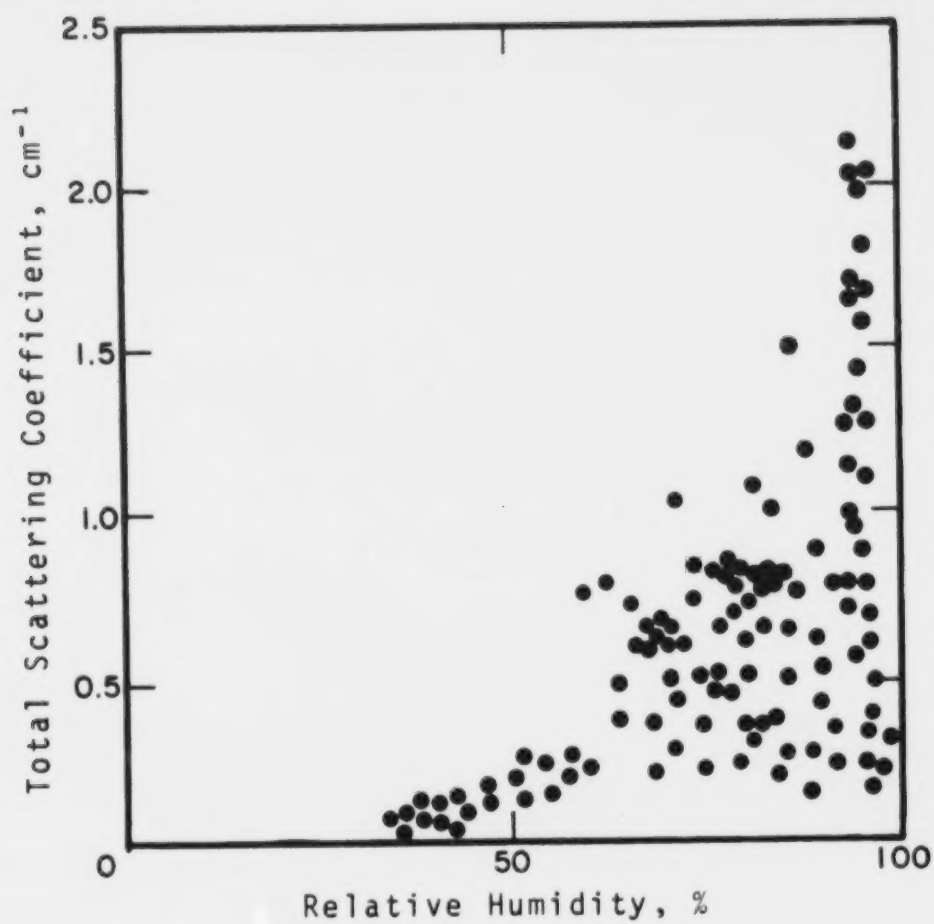


FIG.5 CORRELATION BETWEEN THE TOTAL SCATTERING COEFFICIENT AND THE RELATIVE HUMIDITY (FROM THE DATA ON SPECTRAL TRANSPARENCY).

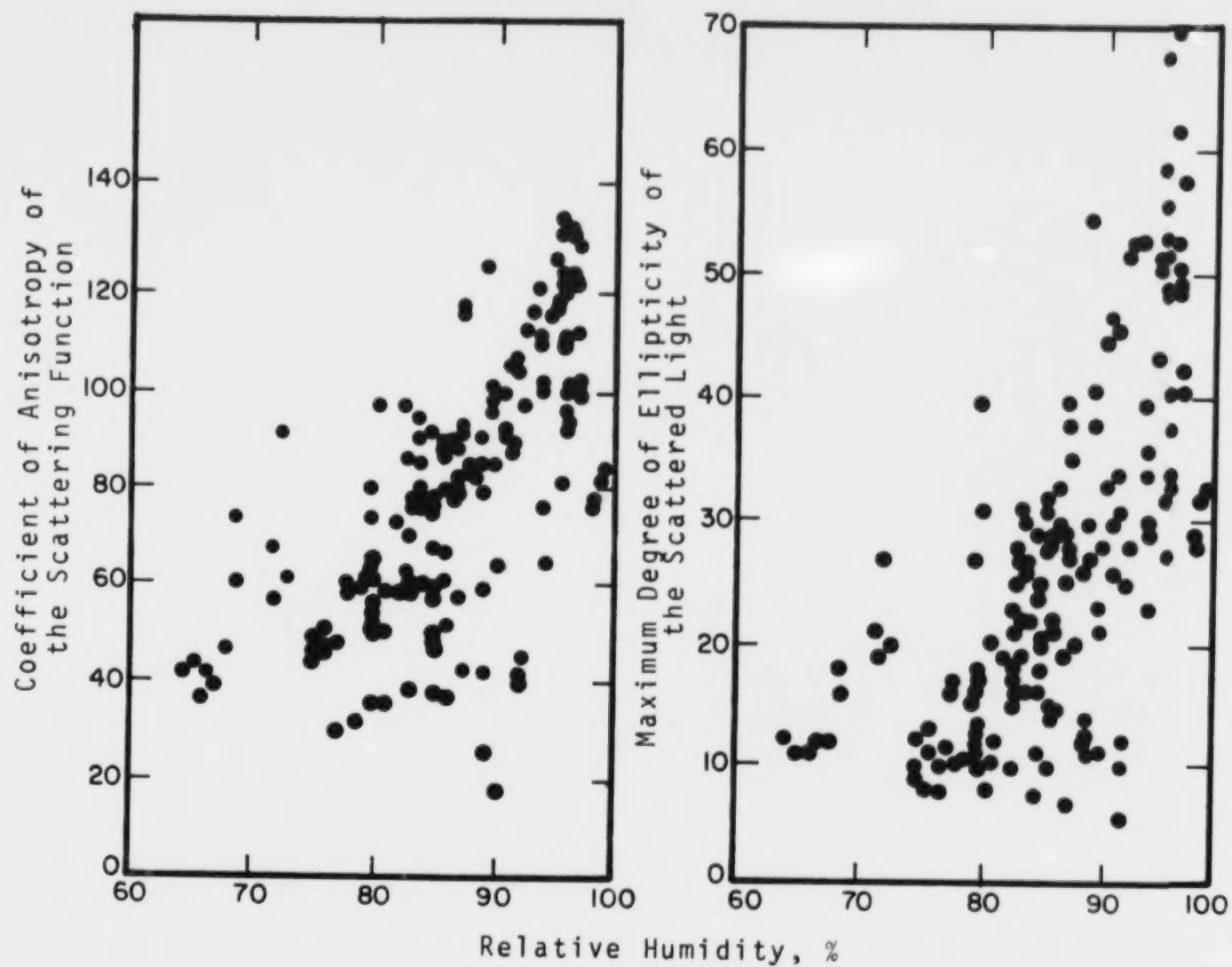


FIG.6 CORRELATION BETWEEN THE OPTICAL PROPERTIES OF AEROSOL AT $\lambda = 0.55$ AND THE RELATIVE HUMIDITY (FROM SCATTERING MATRIX MEASUREMENTS).

On the basis of this material, together with the analysis of correlations between various components of the scattering matrix [107,108,109,274], and of the nature of deformation of the scattering function accompanying the increase of the scattering coefficient, Rozenberg suggests the following pattern of haze formation:

The initial fraction of dry Aitken nuclei is practically unnoticeable in the optical sense. But, as the relative humidity reaches 30% - 40%, the condensation nuclei acquire water shells and their largest fraction moves into the optically active region (0.1 - 0.3 μ). This leads to a sharp increase of atmospheric turbidity. The growth of particles at this state is mainly due to condensation and is characterized by a steady increase of particle's size while the total concentration remains practically constant.

As the relative humidity becomes greater, a qualitatively new phenomenon arises - a 'dense haze'. It is accompanied by the formation of at least two stable fractions of large and giant particles (1-5 μ and 12-15 μ) - the first fraction manifests itself in rainbows; the second fraction determines the aureole part of the scattering function. At the same time, the particles responsible for "haze" (0.1 - 0.3 μ) disappear [61,107]. This can probably be interpreted as a result of coagulation or the condensation transport of water from smaller to larger particles.

This picture is confirmed by the results of Wagman *et al.* [365], who have performed detailed studies of particle size-distribution of sulfate components in four urban areas. Their examples of correlation between the mass median diameter (MMD) and the relative humidity (see Fig. 7) reveal the same tendency of the size-distribution curve to shift toward large particles as humidity increases. It is most interesting that this result was obtained

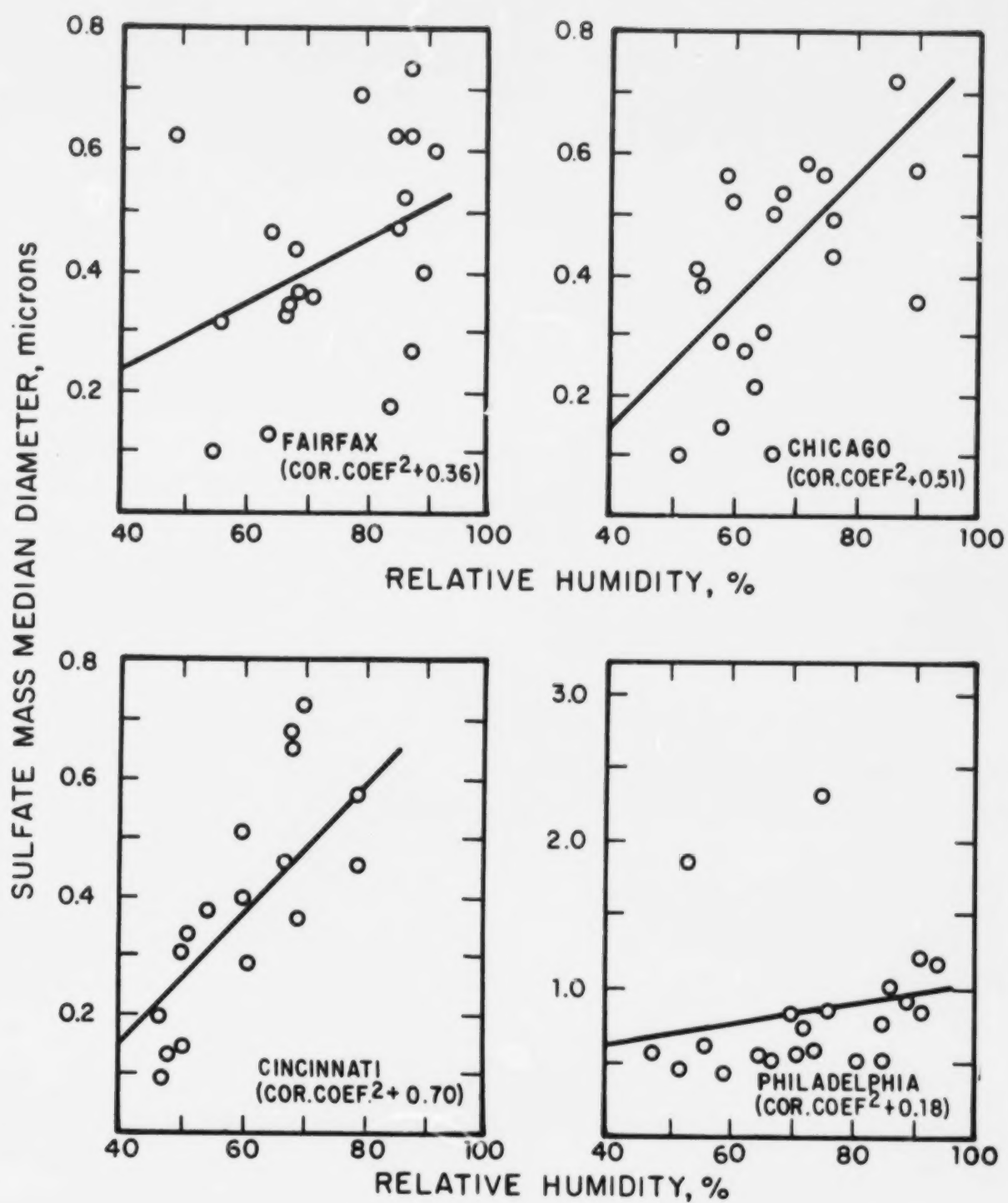


FIG.7 VARIATION OF SULFATE MMD WITH RELATIVE HUMIDITY. LINEAR REGRESSIONS AND ASSOCIATED CORRELATION COEFFICIENTS FOR THE DIFFERENT SAMPLING SITES ARE SHOWN.

with inertial separation in an Andersen cascade impactor (i.e., by a nonoptical method) in the size range of optically active particles ($0.1-0.8\mu$). It is therefore an independent confirmation of the pattern suggested in [271].

The study of events on a microscopic scale has been intensively pursued both in relation to general aspects of aerosol dynamics and out of pure microphysical interest. Perhaps the best up-to-date monograph in this field now is that edited by Davies [51], in which the chapters are written by leading authorities in their areas. The chapter on coagulation contains a discussion of thermal coagulation for both spherical and nonspherical particles, coagulation in the presence of inter-particle correlation, coagulation in external force fields, etc. A considerable part of the book is devoted to the behavior of aerosols in electric fields, photophoresis, diffusophoresis, filtration, etc.

Other important sources of information on modern research in aerosol microphysics are the materials of the VI International Symposium on Condensation Nuclei (Albany, N.Y. and University Park, Pa., USA) [143], of the First National Conference on Aerosols (Liblice, Czechoslovakia) [79], and the book of Amelin on the theory of fog condensation [7].

In conclusion of this Chapter, we present a summary table on the most important chemical processes involved in haze formation.

TABLE IX. Summary of Atmospheric Chemical Interactions of Significance in Haze Formation.

Reactions	Importance
$\text{SO}_2 + [\text{O}_2] + \text{H}_2\text{O}$ Catalyst H_2SO_4 in solution	Possible means by which most sulfur-bearing gases ultimately become converted to SO_4^- in natural and urban atmospheres. No sunlight is needed. This reaction may be responsible for producing sulfates which become cloud and fog nuclei.
$\text{SO}_2 + h\nu \rightarrow \text{SO}_2^*$ $\text{SO}_2^* + \text{O}_2 \rightarrow \text{SO}_4$ $\text{SO}_4 + \text{O}_2 \rightarrow \text{SO}_3 + \text{O}_3$	May occur in polluted atmospheres in sunlight.
$\text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_2 + \text{M}$	May occur in natural and polluted atmospheres in sunlight. May account for formation of stratospheric sulfate particles.
Olefin + NO_2 + $h\nu$ oxidant, particles [see reactions (1)-(31)]	Produces natural hazes when olefin is terpenoid compound. Produces photochemical smog with olefins from automotive exhausts.

E. Recommendations

1. It is recommended that the suspended particulate materials in natural and urban atmospheres be analyzed chemically so that at least 90% of the mass be accounted for. This could be done for one sample a week for each of the NASN stations as a start.
2. The amounts and structures of the carbonaceous and organic components which apparently comprise much of the mass of suspended particulate matter in all atmospheres, natural and polluted, should be further studied and elucidated.
3. It is recommended that investigations of the compositions, variations with vegetation type, and amounts produced of terpenoid compounds be studied. Estimates of global emissions and the prevalence of natural hazes should be made.
4. Efforts should be expended to study the composition of the Aitken nuclei fraction of suspended particulates in both clean (natural) and urban atmospheres. This is of importance in understanding (a) the processes of droplet nucleation and growth and (b) the possible role of gaseous materials which may be associated with the Aitken nuclei. This last aspect would involve laboratory studies.
5. Since the formation of fogs and hazes in marine environments may be influenced by land-generated particles, including pollutant particles, it is recommended that further studies *in situ* be made to strengthen our knowledge of the possible interactions. This would involve systematic sampling and analyzing filter samples and individual droplets with their associated nuclei. A minimum of two stations with contrasting climates should be chosen and routine studies should be

carried out for at least two years. The more stations studied and the longer the time the better and the more reliable the information will be.

6. It is recommended that more detailed studies be performed of the rate of photo-oxidation of sulfur dioxide. In effect, this would include performing an experiment similar to that of Gerhard and Johnstone with improved techniques.
7. The role of SO_2 and its reactions in the formation of photochemical smog should be more clearly understood. Both field and laboratory studies could shed further light on these matters. Specifically, investigations should be aimed at answering the following questions:
 - (a) If Goetz and Pueschel are correct, why are there differences in the volatility of aerosols formed with and without SO_2 present?
 - (b) Does SO_2 or H_2SO_4 act as a catalyst in formation of photochemical smog?
 - (c) To what extent does SO_2 become converted to sulfur-bearing organic compounds in photochemical smog formation?The answers to (b) and (c) will aid in answering the more encompassing question (a).

It is recommended that laboratory studies aimed at solving the NO to NO_2 conversion problem be performed. This is perhaps more easily said than done. However, it is felt that kinetic studies of various NO , O_2 , and olefin systems may prove fruitful. The possibility of singlet oxygen playing a significant role should not be overlooked.

IV. DISTRIBUTION AND DYNAMICS OF ATMOSPHERIC AEROSOL

A. Dynamics of the Size Distribution of Aerosol Particles

Empirical expressions for aerosol size spectrum. The most important characteristic of aerosols is the function that characterizes the number of particles of a given size. If determined correctly, this function can indicate the origin of the aerosol, its surface properties, its density, etc. Since the processes that lead to a given size distribution (dispersion, coagulation, sedimentation, diffusion, etc.) are extremely difficult to account for in a quantitative manner, continuous attempts have been made to present experimental results by means of a simple analytical expression [268,269]. Apparently the most flexible empirical formula is the one that contains a power function together with an exponent; the third parameter depends on the total concentration of particles:

$$dn = a r^b e^{-cr} dr . \quad (1)$$

The suggested distributions of Roller [268], Rosin-Rammler [269] and Junge [151] can be regarded as special cases of the above formula.

Varying the parameters b and c can help to describe the fine fraction of aerosols in a clear atmosphere (the Junge part of the spectrum) as well as the sea spray aerosols and cloud droplets, with the maximum of the distribution curve shifted towards larger particles.

Deirmendjian [53] suggested a rough classification of different types of aerosol atmosphere: a continental atmosphere with a Junge-type distribution, a maritime haze with $dn \sim r e^{-b\sqrt{r}} dr$, and cloud droplets with $dn \sim r^6 e^{-1.5r} dr$.

Another popular empirical formula is that of the lognormal distribution:

$$dn \sim \frac{1}{\sqrt{2\pi} \cdot a} \exp - \frac{(\log r - b)^2}{2a^2} d \log r . \quad (2)$$

This law was confirmed in [85,124,184,252,359] for cloud droplets, mists, solid aerosols and sulfuric acid droplets. Kolmogorov [165] has obtained the lognormal distribution from simple assumptions on dispersion of solid materials.

Friedlander's theory. The usual procedure of presenting the data on size distribution in logarithmic or double logarithmic scale tends to conceal the differences between the results of individual measurements. Therefore, attempts to interpret the experimental values of the size distribution in terms of empirical formulae similar to Eq. 1 or 2 should be regarded as descriptions of the average properties of the distribution curve under very generally defined conditions. In order to catch local variations of the particles' sizes (produced, for example, by a sudden change of humidity or the chemical composition of condensation nuclei or by variations in the turbulence regime), one must undertake a deeper analysis of the elementary processes that produce a given size distribution. In this sense, one cannot overlook a series of papers [42,83,84] in which the authors deduce the shape of the size distribution on the basis of equilibrium between coagulation and sedimentation processes.

Historically, the paper of S.K. Friedlander [83] appeared first in this series. He presents an equation describing the dynamics of the aerosol distribution function in terms of the rates of coagulation and settling. The expression for coagulation rate is borrowed from Smoluchowski [315], who had obtained it from

a steady state solution of the diffusion equation. (The rate of settling is expressed through the Stokes-Cunningham settling velocity).

The subsequent analysis by Friedlander of the resulting integrodifferential equation is made on the basis of two simplifying assumptions: (1) that the upper end of the spectrum has reached a state of the so-called local dynamic equilibrium (in every elementary air volume the rate at which matter enters from the Aitken range is equal to the net loss by sedimentation), and (2) that the shape of the upper end of the spectrum is completely determined by the Smoluchowski's coagulation constant, the ratio of the particles' density to the air viscosity, and by the rate at which the matter enters the upper end of the size distribution.

By making use of dimensional argument, the author suggests two expressions (power laws) for two different subranges at the upper end of the spectrum; these expressions are supposed to be of universal nature and to provide an adequate description of the said portion of the size distribution curve under various local conditions.

The approach of Dr. Friedlander, while being most progressive from the point of view of aerosol physics as it contains attempts of a consistent theoretical analysis of the field data, is still open to doubt. The most important objection seems to be that the results of Smoluchowski's formalism are applicable only for particle systems suspended in a motionless gas or in a gas in the state of laminar flow. Therefore, the process of turbulent diffusion is completely ignored.* One obvious consequence of taking

*This circumstance is most surprising as the author is apparently well familiar with other aspects of turbulence theory (the turbulence energy spectra of Batchelor, van Karman and Lin, similarity theory of Kolmogorov, etc.).

turbulent diffusion into account would be the destruction of the concept of local dynamic equilibrium. Indeed, with the scale of turbulent mixing going all the way down to millimeter distances, it is difficult to imagine an elementary volume which is sufficiently large to contain a statistically stable number of particles and, at the same time, is small enough to ignore its deformation in the fluctuating velocity field of a turbulent atmosphere.

From the mathematical point of view, the neglect of the temporal derivative of the average concentration which is an immediate consequence of the local equilibrium hypothesis is obviously incompatible with the formalism of turbulent diffusion (see Eq. 6 on page 71).

To illustrate the similarity argument at the upper end of the spectrum, Friedlander [84] undertakes an analysis of experimental material obtained by Woodcock [377]. Unfortunately, the author's derivation of the expression for the volumetric sedimentation flux (Eq. 34 of Ref. 84) contains a mathematical error which can be easily traced from dimensional considerations. Indeed, in Friedlander's notations, the dimension of $f/(4\pi \cdot S)$ is L^2 whereas the dimension of $n^5 dN$ is L^{-23} . This error is carried over to the next line of Eq. 34 of Ref. 84 since the author has used the formula

$$m = \rho \left(\frac{4}{3} \pi n^3 \right) \quad (3)$$

from page 126 of Ref. 84 to express the quantity n^5 .

The correct form of Eq. 34 in Ref. 84 is

$$f = - \frac{4}{3} \cdot \pi S \int_0^\infty r^5 dN . \quad (4)$$

(The meaning of the symbols on this page corresponds to Friedlander's paper. It is not preserved in the rest of the Report.)

This error renders invalid Friedlander's analysis of Woodcock's data, the only would-be experimental support of Friedlander's similarity theory for the upper end of the spectrum.

The work of Hidy [127,128], Hidy and Brock [129], and Hidy and Lilly [130] contains a quantitative development of the same ideas. Hidy [128] has shown by numerical experiment that indeed after a certain time (about three times the dimensionless coagulation time), a self-preserving function of the size distribution develops. This function was found to be independent of the initial distribution after a sufficiently long time. The equation in question is of the same type as the one analyzed by Friedlander.

Hidy *et al.* present detailed quantitative data on the shape of the asymptotic distribution and its variation with the mean free particle's path and its radius. A good agreement was found between the results of numerical experiment concerned with the average cumulative distribution and the experimentally determined spectrum [331] in colloidal solutions.

Turbulent diffusion and the formalism of general balance.

The effort described, although undoubtedly useful for the problems of colloidal chemistry, still cannot satisfactorily describe the dynamics of atmospheric aerosol since, as was already pointed out, it does not include the phenomenon of turbulent diffusion.

This latter effect has been accounted for in a most exciting series of papers by Levin and Sedunov [184,185,186,288]. The authors have formulated an equation which described the drop size distribution $n(r,t,x_j)$ as a function of particle size (r), time (t), and spatial coordinates (x_j). This equation includes the effects of sedimentation, collision, condensation and turbulent mixing in a random velocity field. Since the system in this case

is clearly nonconservative, it was necessary to generalize the derivation of the semiempirical equation of turbulent diffusion for nonconservative substance. The resulting equation is

$$\begin{aligned} \frac{\partial n}{\partial t} + \left(u_1 - v \delta_{13} \right) \frac{\partial n}{\partial x_1} + A u_3 \frac{\partial n}{\partial r} = & \frac{\partial}{\partial x_1} \left(K_{1j} \frac{\partial}{\partial x_j} n \right) + \frac{\partial}{\partial x_1} A K_{13} \frac{\partial n}{\partial r} \\ & + A K_{13} \frac{\partial^2}{\partial x_1 \partial r} n + A^2 K_{33} \frac{\partial^2 n}{\partial r^2} \\ & + \phi_1 + \phi_2 + H(n, n) . \end{aligned} \quad (5)$$

Here u_1 is the average wind velocity; v , the velocity of sedimentation; δ_{13} , the Cronecker symbol; K_{1j} , the turbulent exchange coefficients; A is a function of the distribution that contains the condensation constants and adiabatic temperature gradients; $H(n, n)$ is the integral of collision, completely analogous to the respective term in equations of Friedlander and Hidy *et al.*; ϕ_1 is the rate of appearance of new drops [186]; ϕ_2 is the rate of transition of condensation nuclei into drops [186].

We have cited this equation because it takes into account practically *all* the relevant processes leading to a given size distribution of an aerosol. By comparison, Friedlander's analysis includes only the truncated second term in the left-hand side of Eq. 5 and the integral of collisions.

The appearance in Eq. 5 of the terms containing both the turbulent exchange coefficients and the derivatives of the size distribution with respect to particle's sizes is related to the fact that the displacement of elementary air volumes by turbulence is accompanied by the change of their physical properties. (The particles are not only being carried mechanically but also being redistributed in the size space.)

An analysis of the one-dimensional model at the early stages of cloud formation (when the drop growth is due mainly to vapor condensation), with the processes of formation of new drops and nuclei-drops transition being neglected, shows that the initial monodisperse spectrum has a tendency to spread into a typical cloud size distribution, shifting its maximum at the same time towards larger particles. Figure 8 illustrates this fact. The calculations were performed for different time intervals at fixed values of the turbulent exchange parameter, condensation characteristics, initial value of the particles' radius, and wind velocity; the sedimentation rate was neglected.

It is a curious fact that the two groups of authors (Friedlander, Hidy, Brock, Lilly and others on one side and Levin, Sedunov, Marin and Belyaev, on the other), working in a completely independent manner and apparently being unaware of each other's efforts, have practically analyzed complementary sets of effects that contribute to the formation of a given size spectrum. While the American group was interested in the balance between sedimentation and coagulation due to collisions, the Russian school performed a detailed analysis of interaction between condensation and turbulent diffusion. Of course, the complete answer to the question how various elementary processes affect the particle's size distribution should be obtained after analysis of the equation of the type obtained by Levin *et al.*, since this equation obviously reflects all the major phenomena related to the spectrum formation. Perhaps a more healthy approach would be to consider the next class of statistical characteristics of the random field of particles' concentration, namely, its correlation functions [i.e., the quantities $\langle n(r_1, x_1, t) n(r_2, x_1, t) \rangle$, $\langle n(r, x_1, t_1) n(r, x_1, t_2) \rangle$, etc.]. Their dynamics would provide information on the matter transfer from one size component to the other, on deformation of the concentration field associated with spatial displacement, and so on.

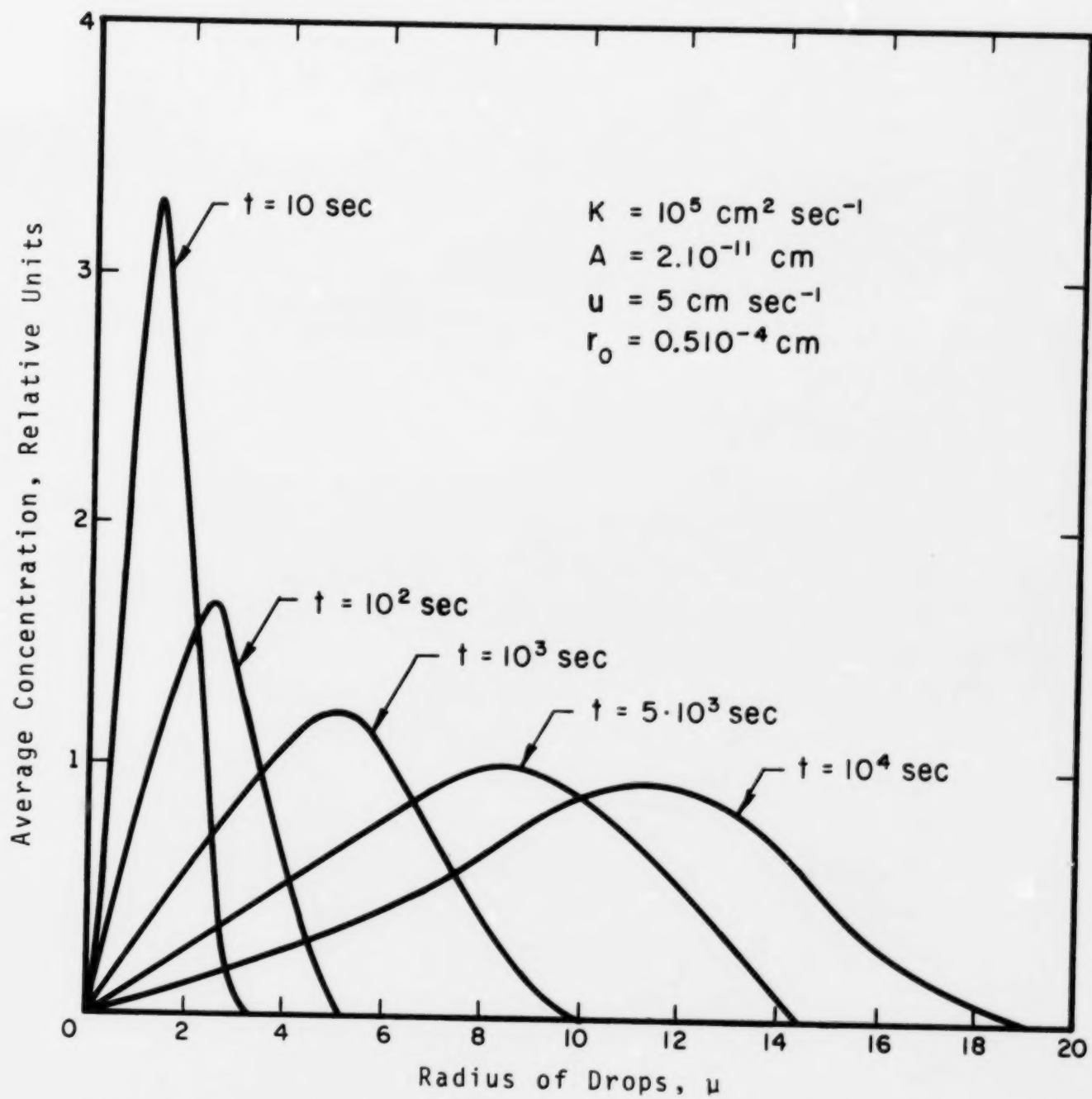


FIG.8 DYNAMICS OF AEROSOL SIZE DISTRIBUTION FROM [49].

The existence and considerable magnitude of short-time random fluctuations of Aitken nuclei concentrations was demonstrated recently by Hogan (Fig. 9), who has presented the results of one-minute averaging for one or two hours of trace length. The pattern on Fig. 9 closely resembles those obtained for turbulent fluctuations in the atmosphere of instantaneous values of wind velocity, temperature, and humidity and thus also suggests the use of a mathematical apparatus similar to the one that was so fruitful in the classical theory of turbulence (see, for example, Ref. 218).

Recent experimental evidence [37,42] seems to confirm the Junge distribution for the lower subrange of the size spectrum and, in this sense, the similarity theory which at this subrange leads to the r^{-4} law seems to have support. When one considers, however, the fraction of larger particles (with $r > 0.2\mu$), no simple regularity of the type suggested by the self-preserving or similarity theory can be observed. (It has to be pointed out that the data reported by Clark and Whitby [42] for large and giant particles were obtained with a Royco PC-200 optical particle counter. The counters of this type [114] are based on the principle that, in a certain size range at the scattering angle of 90° , the scattered intensity is proportional to the particle's cross-section area. This is valid, however, only for particles of optically uniform material; slight variations of refractive index are sufficient to cause variations of intensity by a factor of two or three. Besides, the whole theory of the instrument is based on Mie formulae and therefore applies only to spheres. If in the case of an integrating measuring device, one can assume some averaging

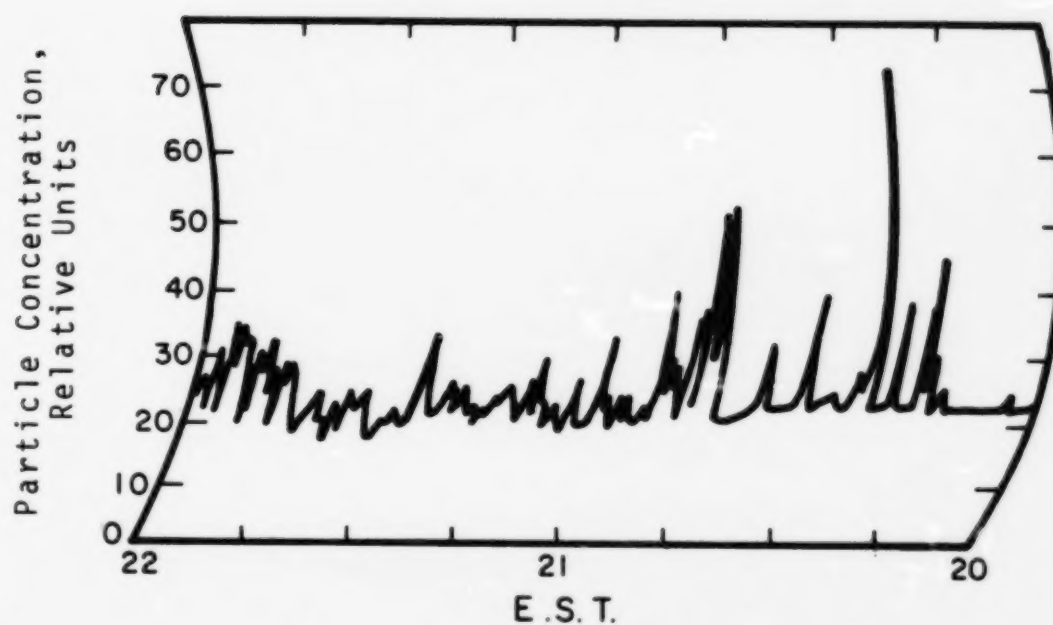


FIG. 9 FLUCTUATIONS OF THE CONCENTRATION
OF CONDENSATION NUCLEI MEASURED
OVER SHORT PERIODS OF TIME.

effects for nonspherical aerosol, a single-particle counter can produce an error of the order of magnitude when it detects a nonspherical body.* As follows from Ref. 37, even under conditions of fog, a considerable fraction of dry aerosols escape capture by water droplets. This fraction, therefore, can completely distort the interpretation of data obtained by particle counters).

Another factor responsible for errors here is, of course, the variation of chemical composition of both wet and dry aerosols. Even if we neglect the latter, without knowledge of the relative concentration of sulfuric acid drops and other liquid chemical compounds, one cannot, at the present stage, rely on the data from particle counters.

Jaenike and Junge [146] have undertaken to establish the presence of the upper limit of the size spectrum which follows from the theory of Hidy and Friedlander. Their investigations, performed with a newly developed free-air impactor for continental aerosols in five different locations, show no upper limit in the aerosol distribution up to the radius of 150μ .

The coarse aerosol was found to be a very regular component of the air and its vertical distribution cannot be accounted for by a sedimentation-diffusion equilibrium.

The same conclusion was arrived at in Ref. 330, in which the author presented the results of morphological identification and chemical microscopical analysis of suspended particulates in Denver (Colorado) air. Wind changes and inversion conditions affected the composition of samples as well as the size distribution.

*A more detailed critique of single-particle counters and the ways of their improvement will be discussed in Chap. VII.

B. Effects of Meteorological Fields on the Distribution of Air Pollutants

It is now universally accepted that the main factor responsible for the spatial dispersion of gaseous or particulate matter in the atmosphere is turbulent diffusion. Irregular motion of air masses associated with atmospheric turbulence has been studied extensively and there exists a fairly well-developed quantitative theory of turbulence supported by numerous experimental data. Since turbulence itself is a manifestation of atmospheric instability, it would be worthwhile to discuss the general features of the hydrodynamic fields in the atmosphere which are characteristic for a particular meteorological situation.

Vertical variation of temperature field. The obvious and well-known effects associated with temperature inversions and other forms of atmospheric stability are most clearly presented in [368], which is also a substantial source of bibliography on meteorological aspects of air pollution.

The author discusses two most significant lapse rates (the rates of decrease of temperature with increase in height): the adiabatic lapse rate for dry air and the same for saturated air. It is the sign of the difference between these and the environmental lapse rate determines stability conditions in the atmosphere. Positive difference corresponds to atmospheric stability.

Vertical gradients of the average wind speed. The distribution of the average wind velocity in the first several hundred feet near the ground is common to all boundary-layer flows in a temperature-stratified medium. The most remarkable feature is the deviation from the Prandtl law which can be related to a certain

temperature stratification of the atmosphere. For unstable temperature stratification, the increase of the average velocity with the logarithm of vertical difference is always more slow than a linear one, whereas in the case of a stable temperature configuration, the increase of the average velocity with the difference of the vertical is faster than the first power. This deviation from the simple logarithmic law becomes more pronounced with the increase of height; it is also more significant for far from neutral temperature stratifications.

The above two main meteorological characteristics (vertical structure of temperature and average wind velocity) determine, to a great extent, the intensity of turbulent pulsations of meteorological elements. The spatial variation of wind and temperature is subject, of course, to diurnal and seasonal variations as a consequence of the changing nature of the radiation balance of the Earth's surface.

Topographic effects and complex studies. Although the most difficult to account for in a quantitative manner, topographic effects greatly influence the occurrence and spatial distribution of hazes. The terrain configuration creates a certain pattern of dominant winds, as well as of convective cells, which in turn determines the rate and nature of turbulent mixing. The local condition of air pollution has been extensively studied during recent years. The questions of interest in these studies are: the predominant local winds [4,81,147,178,179,180,183,221,230,231,232,280,283,284,285,293,324,333,370,371]; the conditions of fog formation [147,232,285]; the onset of chemical hazes [285]; distribution of sources of oxidants [147,183]; the radiation regime [283]; the visibility range [98]; recurrence of local temperature inversions (hot and sultry weather) [4,98,147,179,180,210,221,232,283,333,357,358]; and descending vertical currents [231,293].

Harada and Goto [120] observed the relation between the local pressure pattern, topography and smog occurrence at Osaka (urban area). The same features of the pressure pattern (low-gradient, quasistationary pressure field) responsible for high concentration of harmful industrial emissions was detected by Shevchuk [293], who studied the aerosynoptic conditions conducive to prolonged periods of the maximum air pollution in Kemerovo. The results of a three-year study (1962-1964) indicate that the anticyclonic or quasistationary filling cyclonic pressure field, with low gradients not only at the stack level but also at the 1 - 2km layer, leads to protracted spells of local air pollution.

The height of the temperature inversion that leads to the maximum concentration of air pollutants also depends on the local factors (it is ~1000m in Hamburg and Gelsenkirchen [98] and ~500 - 600m in Kemerovo [293]).

Among the recent papers summarizing information on the role of meteorological factors in air pollution, we have to mention, apart from [368], Weedfall's mesoclimatological classification system for air pollution engineers [370]. The author has reviewed the standard climate classifications and other methods of presenting climatic data. Through the use of national maps, an analysis of wind speed, relative humidity and sky cover data was performed for 129 different airport locations. A general stagnation index for primary pollutants, as well as other indices for photoreacting and fog-reacting pollutants, was obtained on the basis of the analysis of mixing height data and the ventilation effect.

The study of topographic effects, including a valley's area, orientation, the ratio of height to width, and aspect of slope, has led to the formulation of potential insulation tables for various parameters characterizing the topographic structure. Some

computations were made for four different valley areas. The author also discusses the relative value of various stagnation indices.

The statistical analysis of ground inversions for the period from 1960 to 1964 was given in [356]. The maximum frequency of inversions was found at night in winter. One of the results was that an occurrence of an inversion is favored by cloudiness and weak winds. There was also observed high correlation between the concentration of air pollutants and ground inversion.

Seven different locations in various climatic regions of the United States were analyzed from the point-of-view of mixing depths, wind speeds, and air pollution potential by Holtzworth [140]. In order to obtain the estimates of meteorological factors (mixing depths and wind speeds), the author used regular surface as well as upper air observations by the Weather Bureau. The frequency of occurrence of various combinations of mixing depths and wind speed classes were used in an urban diffusion model to calculate theoretical values of relative pollutant concentrations for four major cities.

A United States Environmental Sciences Service Administration [320] study attempted to set up a forecast program to determine the air pollution potential, defined as a set of meteorological conditions conducive to the accumulation of atmospheric pollutants. Such conditions are taken into account over the large scale in schematic terms. A description is given of particular numerical subjective means by which the high air-pollution-potential conditions can rapidly be detected and forecast.

A study of meteorological influences on air pollution over cities performed by Sonkin *et al.* [317] found that a relationship between wind speed and atmospheric pollution in the warm and cold

half of the year manifests the following characteristics: There is a distinct correlation between the concentration maxima and the wind speed. One of the maxima occurs during calm weather and the second occurs at a wind speed of 4 - 6 m/sec.

In winter the former maximum is greater than the latter; in summer the second maximum is more pronounced. The traditional correlation between high concentration of air pollutants and anticyclonic pressure field is more marked during the cold half of the year. A similar study of the meteorological effects of the lower level air pollution from ships over selected New England ports was performed by Cormier [44].

A certain degree of attention is paid to the measurement of the vertical distribution of hazes [161,187,188,229]. In [187,188], the authors present the results of measurements performed during 80 helicopter flights over two distinctly different geographical areas (the urban district of Gazli and the Tien Shan Mountains). The dynamics of the upper and lower boundary of the haze region was studied in relation to temperature gradients.

Aircraft analysis of the vertical distribution of various haze constituents [161] has shown that concentration of the solid aerosols decreases rapidly with height, whereas in the case of gas pollution the vertical decrease is not so pronounced. In many cases the highest concentration of the gaseous component occurs at an altitude of several hundred meters. Generally over industrial areas, the pollution has a vertically stratified pattern.

C. Diurnal and Seasonal Variations of Air Pollutants

Urban atmospheres. The daily cycle of atmospheric particulates has been studied recently for both polluted [42,59,312,327,

365] and unpolluted atmospheres [135-137]. In urban areas with relatively high industrial and traffic activity, the majority of authors agree to see two main maxima—one shortly after sunrise and the other near or just after the sunset. A detailed study of the behavior of this cycle in terms of soiling index (which apparently reflects the total mass content per unit volume of the solid fraction of particulate air pollutants) was performed by P.W. Summers [327]. He collected data from three meteorological stations situated inside central Montreal and in its surroundings; he also performed simultaneous wind and temperature measurements at these locations. Figure 10 shows the air pollution daily cycle observed in May, together with average wind and temperature variations. A similar diurnal cycle was obtained for each month of the year. An elementary analysis of these curves has shown that they can be classified into two types: one of them (type A) is characteristic for winter months from December through March; the other one (type B) corresponds to a large daily range with the morning peak considerably higher than the evening one. This type of cycle occurs during the remainder of the year.

Qualitatively, the same pattern was reported by Sladek [312] who measured the diurnal regime of atmospheric pollution by sulfur dioxide in Prague. He also found that the morning maximum which occurs in the same time period of the day throughout the year, exceeds the evening maximum during spring, summer, and autumn. Both authors have noticed pronounced difference between the weekday and weekend patterns — mainly in terms of concentrations. The reduction of the soiling index reported by P.W. Summers for Saturdays and Sundays constitutes 25% and 32%, respectively, of the average weekday figure. Other authors [113, 206, 219, 220, 387] have observed similar effects in Leicester (England), Ottawa, Vancouver (Canada), Paris, and Toronto. The general shape of the Saturday curve was

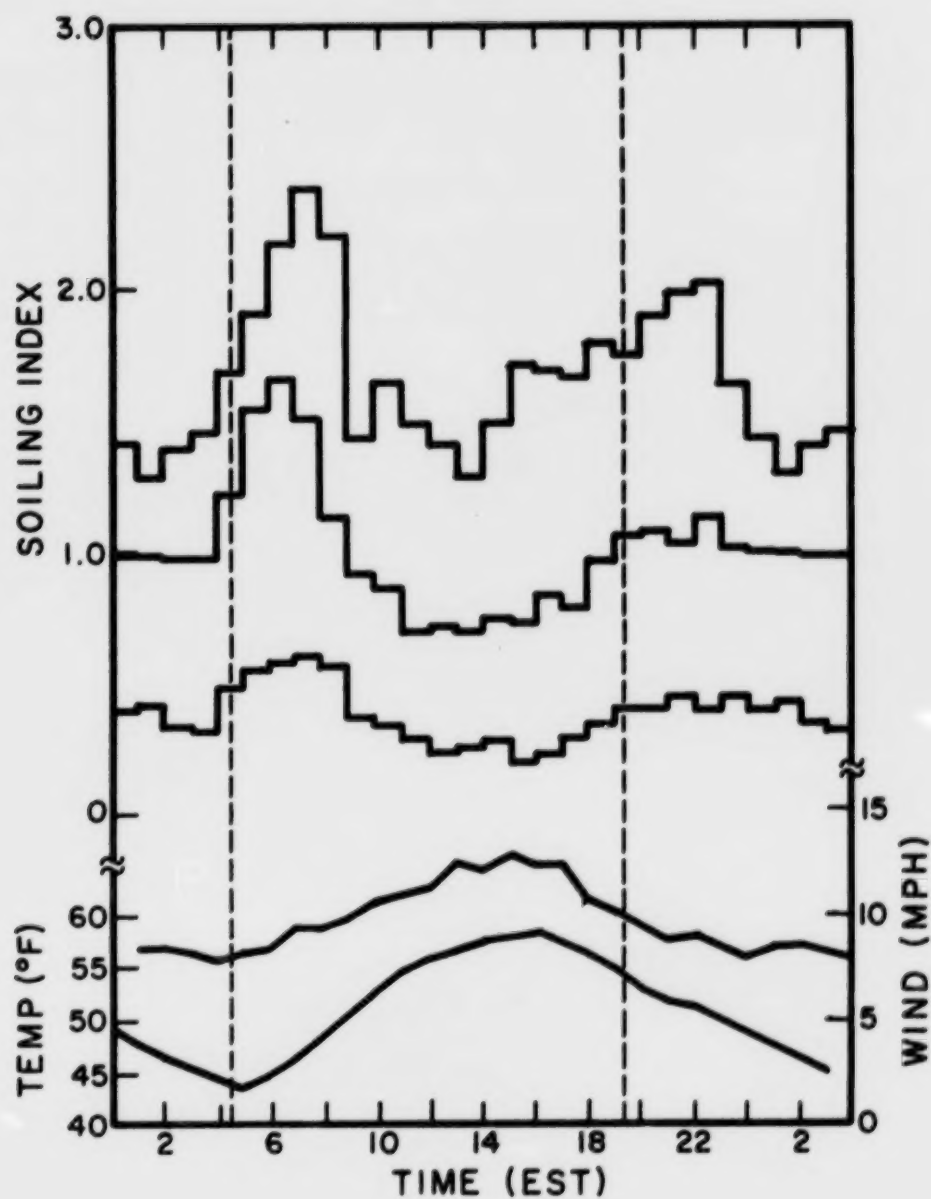


FIG.10 THE MEAN WEEKDAY DIURNAL CYCLE OF SOILING INDEX, WIND SPEED AND TEMPERATURE FOR MAY. THE THREE HISTOGRAMS CORRESPOND TO THREE DIFFERENT LOCATIONS (IN URBAN AREA).

found to be very similar to the weekday pattern, the reduction being spread uniformly over the day.

Clark and Whitby [42] who have performed size-differentiating studies of atmospheric aerosol at a university campus, have registered the two-maximum pattern for each fraction.

The explanation of the main features of the observed cycles [327] is based on conditions of changing equilibrium between the rate of smoke production by industry and traffic and degree of ventilation which depends on the height of mixing depth and other conditions determining the order of instability of the atmosphere. The reason for the evening peak being relatively higher in winter than in summer is that in winter the late afternoon ventilation decreases before the slowdown of production rate while in summer the reverse is true.

Somewhat at a discrepancy with these results is the work of Wagman, Lee, and Axt [365] who have measured the diurnal variations of sulfate particulate concentrations in Cincinnati, Chicago, Philadelphia, and Fairfax (Ohio). According to their results, there was no consistent periodic pattern in the diurnal trends in sulfate concentrations for these locations. A possible explanation of this lack of consistency would be a rather large time interval (8 hours) used for averaging the results for sulfate concentrations to derive the diurnal trends. A shift of the morning maximum to 10.00 (towards the 'midday' range) can easily conceal the two-maximum pattern.

Natural atmospheres. A completely different cycle exists in nonpolluted atmospheres [22,25,135-137], in terms of concentrations of Aitken nuclei. When not influenced by diurnal land-sea breezes or local sources, this cycle demonstrates a gradual decrease from

midnight to the approximate time of sunrise; sharp rise to mid-morning; broad maximum from midmorning to mid- or late afternoon; and decrease through evening (see Fig. 11). There are indications [135] that the major factor responsible for the formation of Aitken nuclei in sparsely populated areas is the conversion of gases to particles by solar radiation.

The visibility measurements performed in various geographical locations [59] show the tendency to agree with the two-maximum cycle of pollutants concentrations for densely populated areas and with the one midday-maximum pattern for locations farther away from industrial sites [40,116]. The seasonal variations of the visibility range reported in [59] exhibit the opposite tendency to that observed by Summers [327] in terms of the soiling index: The variability range of visibility in winter was larger than in summer. Apparently, the seasonal and diurnal variations in humidity being imposed on those of solid particulates can modify the seasonal behavior of diurnal visibility cycle toward smaller variation range in summer.

D. Recommendations

1. As follows from Sec. A of this Chapter, the size spectrum is an extremely important characteristic of aerosol from the point of view of indicative its origin and chemical composition. It is therefore recommended that the measurements of the size distribution of all aerosol systems, interesting from the point of view of air pollution, be carried out and the results be approximated by one or two simple empirical formulas. Then each specific particulate pollutant will be characterized by the range of variation of parameters in these formulas. A section of the future haze classification table might look as follows:

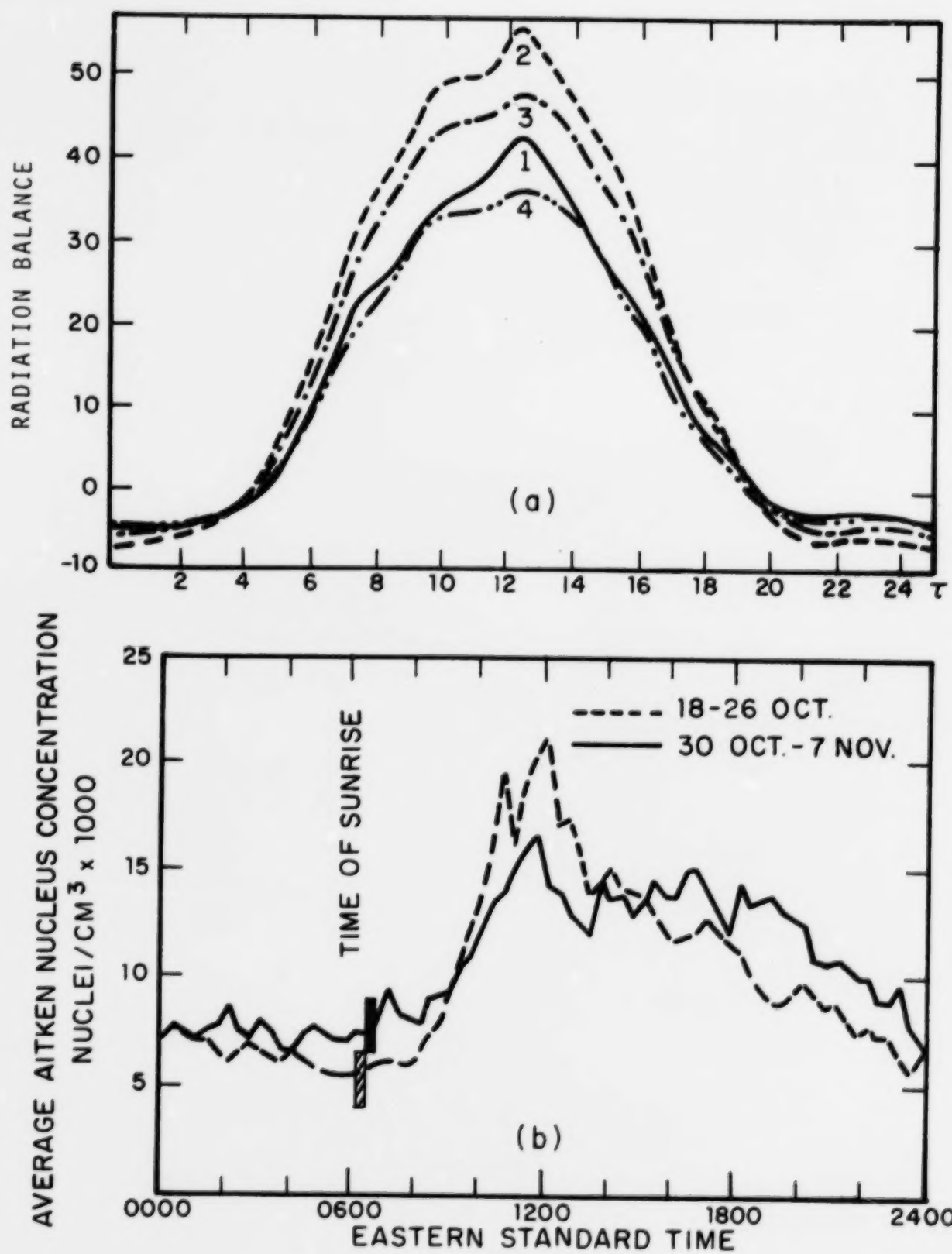


FIG. 11 THE AVERAGE DIURNAL CYCLE OF (a) THE RADIATION BALANCE; (b) CONDENSATION NUCLEI CONCENTRATION AT CRAWFORD HILL OBSERVATORY.

Location	Chemical Composition	Origin	Size Spectrum	
			Γ -Distribution	Lognormal
Urban regions	Sulfates	Oxidation of SO_2 from combustion	$a_1 < a < a_2$ $b_1 < b < b_2$ $c_1 < c < c_2$	$a_1 < a < a_2$ $b_1 < b < b_2$

2. The problem of next priority is that of solving the dynamic equation of general balance; numerical solutions should then be compared with empirical formulae. This analysis will allow to establish quantitative relation between the state of the atmosphere (wind field and turbulent exchange coefficients), certain parameters indicative of the chemical composition (condensation constants) and the size distribution. Then it will be possible to specify further the aerosol nature (e.g., from known size distribution and the state of the atmosphere, to deduce the chemical composition).
3. Importance of measuring the temporal (diurnal) variations follows from these facts: (a) Only they could allow to distinguish between natural and antropogenic sulfates and nitrates. (b) Temporal variation of size distribution together with relative humidity allows to separate the portion of the particles that acts as condensation nuclei.
4. From the point of view of interaction between various size fractions of the aerosol spectrum, it appears worthwhile to develop a general statistical approach to the problem - e.g., to consider higher-order moments of the random field of aerosol concentration.

V. QUANTITATIVE ANALYSIS OF TURBULENT DIFFUSION

Classical treatment of the mathematic aspects of turbulent diffusion theory [12,82,217,218,233,329] is based essentially on the assumption that in regions free from the sources of the admixt, its concentration field $n(x,t)$ satisfies the equation of molecular diffusion

$$\frac{\partial n}{\partial t} + \frac{\partial(u_{\alpha} n)}{\partial x_{\alpha}} = \chi \Delta n \quad (6)$$

with certain boundary conditions. In Eq. 6, χ is the coefficient of molecular diffusion; u_{α} is the α -component of wind velocity.

For homogeneous boundary conditions, the time evolution of the admixt concentration is determined only by the material transport in the velocity field and by molecular diffusion. Under general assumption [218], average concentration can be obtained from the equation

$$\bar{n}(x,t) = \int P(x_1|x,t) n_0(x) dx \quad (7)$$

where $P(x_1|xt)$ is the Green function of the averaged equation of turbulent diffusion and $n_0(x)$ is the initial distribution of admixt concentration.

In the case of a stationary linear source parallel to the axis OX_2 and of the average wind u directed along OX_1 , it follows from the formalism developed by Monin and Yaglom that the average thickness of the plume downstream with respect to the linear source increases for small distances as the first power of the horizontal distance, and for larger distances as its square root. This fact was confirmed in a series of experiments [154,344,350]. The shape

of the plume behind a point source is first conical and later becomes that of paraboloid of rotation.

A. The Semiempirical Diffusion Equation

Quantitative comparison between the rates of turbulent and molecular diffusion shows that the latter process can be nearly always neglected in atmospheric conditions. Indeed, the "turbulent diffusion coefficient," D (i.e., the ratio of the turbulent flux to the concentration gradient) is of the order of $10^4 - 10^5$ cm²/sec whereas the molecular diffusion coefficient χ for most atmospheric gases is $\sim 10^{-1}$ cm²/sec; χ is, of course, much less for the particulate matter.

This justifies the use of the so-called 'semiempirical' diffusion equation [279, 280], which can be obtained from the transport equation (6) by putting $\chi=0$ and by assuming that the average density of the turbulent flux of the admixt $\sigma_\alpha = \overline{u'_\alpha n'^\dagger}$ is proportional to the gradient of the average concentration:

$$\sigma_\alpha = -K_{\alpha\beta} \frac{\partial \bar{n}}{\partial x_\beta} . \quad (8)$$

In this equation the matrix $K_{\alpha\beta}$ (the matrix of the turbulent diffusion coefficients) can depend on coordinates and time.

In the case of a stationary and homogeneous turbulence and the average wind velocity $\bar{u}$ directed along Ox_1 , the semiempirical equation of turbulent diffusion is

$$\frac{\partial \bar{n}}{\partial t} + \bar{u} \frac{\partial \bar{n}}{\partial x_1} = K_1 \frac{\partial^2 \bar{n}}{\partial x_1^2} + K_2 \frac{\partial^2 \bar{n}}{\partial x_2^2} + K_3 \frac{\partial^2 \bar{n}}{\partial x_3^2} . \quad (9)$$

[†]The prime in this notation means fluctuating quantities.

This is the main mathematical tool to study the quantitative aspects of turbulent diffusion. Note that in this model the average wind, as well as the turbulent exchange coefficients K_j , depend only on the height above the ground.

Roberts' model. The solution of Eq. 9 can be obtained in a closed (analytical) form only for special cases of the wind and the turbulent exchange profiles. The development of quantitative knowledge in this field started with the work of Roberts [265] who considered the simplest case of constant $\bar{u}$, K_j . He solved the semi-empirical diffusion equation with the boundary conditions corresponding to 'reflection' and 'absorption' at the earth boundary for an elevated instantaneous point source. On the basis of his results, one can easily obtain [157] the distribution of the admixt concentration in the case of a stationary point or linear source. According to the exact solution of the semiempirical diffusion equation, in Roberts' model the rate of decrease of the concentration at the earth level with the horizontal distance from the source corresponds to the law $\sim x^{-1}$ for the stationary point source and $\sim x^{-1/2}$ for the stationary linear source. These results have not however, been confirmed in field experiments [223,329].

Vertical variation of meteorological fields. This discrepancy can be, of course, the consequence of the oversimplified nature of the Roberts' model. In reality both the wind velocity and the turbulent exchange coefficients have a tendency to increase with height. A more consistent approach which takes these variations into account encounters however serious mathematical difficulties. The most popular technique now seems to be that of separation of the process of vertical diffusion from the horizontal spreading. In this formalism the total mass of admixt θ at a certain height Z satisfies the two-dimensional diffusion equation

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x_3} \left[K_3(x_3) \frac{\partial n}{\partial x_3} \right] \quad (10)$$

Solutions of this equation together with the initial condition corresponding to an instantaneous point source and a homogeneous boundary conditions on the ground were obtained by Laihtman [171]; later they were investigated for various meteorological situations by Monin [216].

Unfortunately, little is known about the variation with height of turbulent exchange coefficients. The following models for $K_3(Z \equiv x_3)$ were analyzed

$$K_3(Z) = K \cdot Z \quad (11)$$

$$K_3(Z) = K \cdot Z^\beta \quad (12)$$

$$K_3(Z) = \begin{cases} K Z & 0 < Z < H \\ \text{const} & H \leq Z \end{cases} \quad (13)$$

In the cases 11 and 12 one can obtain the analytical expressions for the vertical distribution of concentration n [218]; model 13 leads to a numerical solution. The concrete type of dependence of K_3 on height should be chosen in agreement with a given temperature stratification. Thus, for a neutral temperature profile (the vertical lapse is equal to the adiabatic one), Monin and Yaglom [218] suggest the model 11; for a slightly stable stratification the model 12 with $\beta < 1$ is more appropriate; in the case of strong stability one has to use Eq. 13. For a slightly unstable atmosphere, formula 12 with $\beta > 1$ is acceptable; in the case of a strong instability it is better to use composite formulae with different power laws for various vertical intervals.

In view of the lack of information on the exact variation with height of turbulent mixing parameters, the recent work of Eliseev [70], which describes the method for determining the vertical component of the turbulent exchange as well as the parameter of horizontal spreading from the visible configuration of a smoke cloud, seems to be well-timed. The author suggests the use of an aircraft for obtaining the information on the shape of a smoke plume and considers various geometries of the mutual orientation of the source, the cloud, and the aircraft. The explicit analytical formulas for the parameters of turbulent diffusion as dependent upon the linear dimensions of the smoke cloud as well as on meteorological conditions, are presented.

The horizontal spread of the admixt can be calculated on the basis of local values of wind velocity and the horizontal turbulent exchange coefficients K_1, K_2 by applying the Roberts' formula for each plane layer of the atmosphere. This method, however, can yield only rough estimates of the effect since it does not take into account interaction between the vertical turbulent exchange and the vertical wind gradient.

Diffusion from stationary sources. For sources that produce a constant amount of admixt at any time, the quantitative analysis is somewhat simpler. The following problems, listed in the order of increasing complexity (and better approximation of real situation) have been solved:

1. Stationary linear elevated source without longitudinal diffusion with constant wind velocity and turbulent mixing increasing with height as the first power of Z [24].
2. Linear source at the ground, the wind velocity and turbulent mixing obey an arbitrary power law [36, 88, 172, 173].

3. Elevated source under the same conditions [172,173,270,314].
4. Elevated linear source in the case of 'partial absorption' on the ground and composite model of the type 10 for the wind velocity and turbulent mixing [172,173,382].
5. Linear source in a logarithmic boundary layer; turbulent mixing varies as the first power of Z (numerical solution) [18,19].
6. Linear source in a universal velocity field.* The turbulent mixing constant is determined by the average velocity gradient and friction velocity. (numerical solution) [379].
7. Diffusion in a thermally stratified rotating atmosphere [155].
8. Diffusion in an atmosphere with an exponentially decreasing density [162].

B. Mathematical Models for Specific Locations

The above discussed theory fails to account for specific terrain and microclimatological conditions, as well as for temporal and spatial variations of the source intensity, which are invariably present in any situation (see also [349]) interesting from the point of view of the air pollution.

In this sense it seems very useful to develop concrete mathematical models for a specific location (or class of locations). An example of work in this direction is the paper of Miller [214], in which the author suggests a mathematical model of atmospheric diffusion for metropolitan areas. The main simplifying assumption of this work is the uniformity of pollutant sources over the urban area; this makes it possible to avoid numerical computations but at the same time limits the value of quantitative predictions of the concentration distribution derived from this model.

*i.e., the velocity profile is given by the similarity law.

Szepesi [332] discussed a numerical technique of solving the diffusion equation for the surroundings of power stations that takes into account the predominant wind directions for a given area. The peculiarity of the pollutants' dispersal in the atmosphere of a coastal zone was studied by Berliand [16,17] who, on the basis of a two-dimensional semiempirical diffusion equation with the boundary conditions corresponding to a set of N stacks, obtained the expressions for the contaminant concentration and the so-called 'dangerous wind speed' at the height of the wind vane. This work contains also the results concerning the influence of the vertical exchange coefficients on the variation of concentration with distance from the source and the flow modelling over hilly terrain in a wind tunnel.

Still more specified models exist now for Denver air pollution [57,67] and the distribution of contaminants in Washington, D.C. [311]. The method in Ref. 57 seems to be most adjusted to the local micrometeorological conditions.

C. Empirical Treatment of Atmospheric Diffusion

Along with a continuous effort towards a deep quantitative understanding of turbulent diffusion, there have always been attempts to construct simple empirical formulae which are suitable, as a rule, only for a given series of measurements. A monograph by Pasquill [233] contains a good amount of the quantitative material developed along these lines. Probably the most important contribution here was made by Sutton [328,329], who has postulated that the distribution of the admixt from an instantaneous point source has a Gaussian shape and dispersions defined by Taylor's formula through the Lagrange correlation functions $R_{ii}^{(L)}(\tau)^*$ of the wind velocity. Sutton's further assumption as to the concrete expressions for these

* τ - temporal separation.

correlation functions allowed him to obtain dispersions $D_{11}^{(L)}(\tau)$ of the admixt distribution in the form

$$D_{11}^{(L)}(\tau) = \frac{c_1^2}{a} (\bar{u} \tau)^{2-b} \quad (14)$$

where c_1 are certain constants and b is a parameter varying between 0.1 and 0.3 (depending on temperature stratification). On the basis of the (assumed) distribution of admixt from an instantaneous point source, Sutton has calculated the average concentrations for stationary point and linear sources. These results were compared with observed values by a number of authors [10,60,125]. As follows from this comparison, the Sutton formula can be fit to match the experimental dispersions only if one introduces anisotropy of parameter n ; but, in this case, the number of arbitrary parameters in Sutton's formulas becomes so large that their adjustment would allow interpretation of practically any field experiment. Another (and probably most important) shortcoming of Sutton's formulas is their incompatibility with basic statistical concepts of diffusion theory; the real Lagrange correlation functions differ considerably from those postulated in Sutton's theory.

Other, more recent examples of simplified approach to turbulent diffusion, can be found in [48,193,287]. These papers with other related material were published in a special issue of the *Atmospheric Environment* devoted to the CERL Symposium on Chimney Plume Rise and dispersion.

One of the advantages of the work in this direction is that it helps to develop an intuitive (physical) understanding of diffusion processes and in this sense it can provide control material for a rough estimate of the validity of a given mathematical model based on more rigorous diffusion equations. One cannot expect

however to obtain from the empirical formulas accurate quantitative information of general significance that would allow tracing of the main characteristics of diffusion processes to variations of meteorological fields, terrain structure, and the specific properties of air pollutant sources.

D. Diffusion Measurements

In the field of experimental work on turbulent diffusion, one can distinguish, in addition to results mentioned in the previous section, two major techniques: (1) measurements of the plume rise and dispersion [110,119,194,195] and (2) measurements of deposition of particles from a continuous elevated source [65,323,324]. Lucas *et al.* [194,195] report probably the most progressive instrumentation system for simultaneous continuous measurement of the contaminant concentration in a range of distances up to 13 km downwind; the rise and the height of the plume as determined by a search light and a lidar and the vertical variation of all meteorological elements (temperature, humidity, turbulence, wind speed and wind direction) up to 187 m above the ground. It is only too unfortunate that the quantitative interpretation of these most valuable data [119] was performed at the level of the empirical expressions obtained by Lucas *et al.* as far back as 1963. From this point of view, the paper of Goroshko [110] in which the author uses the results of a rigorous diffusion theory for the case considered by Berliand [17, 18] achieves a better understanding of similar experimental data.

Three of the investigators from the second group [16,48,323, 324] used a continuous point source and carried out simultaneous meteorological measurements, in [323], an attempt is made to compare the results with relatively little known flow theories of

Denisov and Csanady. It remains an open question how these theories are related to the universally accepted concept of turbulent diffusion.

Deposition of aerosol from an elevated *linear* source [65] imitated by the author by means of an aircraft equipped with a sprinkler was studied in relation to the relative weight and the rate of deposition for different aerosol fractions, the density of deposition of drops of varying diameters at different distances from the line of dispersal, and meteorological conditions. No serious quantitative analysis was given, but the author presented a discussion of the effect of the three-dimensional spatial and temporal variation of meteorological elements on dispersion.

In conclusion, it would be appropriate to mention the papers [8,94] which contain a quantitative investigation of a complex of mechanisms responsible for contaminant spatial distribution (convective storms, particle's capture, evaporation, dilution, coagulation, precipitation, and turbulent exchange).

The efforts along these lines, the final ambition of which is to create an adequate mathematical formalism for description of the general balance of particulate matter in the atmosphere, most important as they seem, are still in a rudimentary stage.

E. Recommendations

1. As follows from this Section, the equation of turbulent diffusion is the most important mathematical tool for predicting the spatial distribution of hazes. In its inverse formulation, this equation can indicate the position and the strength of the source once we know the distribution of aerosol concentration. It is therefore recommended that the

algorithms for numerical solution of the turbulent diffusion equation be developed for arbitrary wind and temperature profile and for arbitrary terrain.

2. It is necessary to accumulate sufficient knowledge of the vertical variations of turbulent exchange parameters and to establish relations between the latter and the local values of meteorological fields. Extensive use of meteorological tower facilities will make such a program feasible. In order to have all the input data, we have to develop fast measuring techniques for determining the instantaneous state of the atmosphere (in terms of vertical and horizontal variations of temperature, wind, and humidity) over each major metropolitan area.
3. It is also necessary to study the approaches to a rigorous solution of the three-dimensional diffusion equation.

VI. OPTICAL PROPERTIES OF AIR POLLUTANTS

A. Transmission and Visibility Studies

Reduction of visibility as well as attenuation of solar radiation are the most obvious manifestations of the presence of aerosol [56]. Experimental and theoretical studies in this field have been recently summarized by Zuev [385], whose monograph includes quantitative data on absorption, scattering, and attenuation of visible and infrared radiation in narrow spectral bands for different geometrical patterns of the source and the receiver positions under a great variety of meteorological conditions. The book also contains a discussion of one of the most important questions in atmospheric optics: the applicability of Bouguer law to the description of the results of experimental investigations of aerosol attenuation.

Another recent monograph of significance is that of Barteneva, Dovgiallo and Poliakova [11]. This book presents experimental investigations on the optics of the lower layer of the atmosphere carried out by the laboratory of Atmospheric Optics of the Main Geophysics Observatory over a ten-year period. One of the aims of the book was to establish relationships between transparency and other meteorological factors. Contents of the volume include: the transparency regime of the atmospheric layer at the Earth's surface, including the frequencies of ranges of transparency of the atmospheric layer at the surface; the annual and diurnal variations of transparency for various points of the USSR in different climatic regions; atmospheric transparency in vertical and horizontal directions; comparison of atmospheric transparency in haze, fog, rainfall, and snowfall zones.

A review paper on atmospheric optics and radiation transfer by Howard and Garing [141] summarizes the effort of American authors during the years 1964-1968. It contains more than 300 references, classified into sections: General Studies; Pyrheliometry; Solar Insolation and Distribution of Daylight; Earth Radiance and Albedo; Sky Brightness and Cloud and Terrain Reflectance Studies; Transmission and Absorption Studies; Scattering Studies; Atmospheric Refraction, Seeing and Scintillation; and Radiative Transfer Studies.

Recent analysis of other general aspects of visibility in atmosphere include: measurements of transparency of the atmospheric surface layer to the radiation of various lasers [383], vertical distribution of horizontal visibility under clouds and within clouds [255], and pure absorption of light by aerosols in the visual and nearest IR region [192]. On the other hand, there is a tendency to link the visibility variations to local conditions: Petriw and Cantor [238] studied the variations of transparency in the Wisconsin area; Fisher [80] measured atmospheric turbidity in Antarctica and compared the results to those obtained at Boulder, Colorado for the corresponding seasons.

A series of measurements carried out by Curcio [49], for wavelengths between 0.4 and 2.3 micron and ranges from 4 to 160 km across Chesapeake Bay (see Fig. 12), gives an example of a complicated spectral behavior of transparency which can probably be interpreted in terms of multimode aerosol size distribution. References 1, 50, 208, 222, 223, 224, and 326 are also devoted to transparency measurements for slant and horizontal paths, performed from the ground and from balloons.

Thus at present we have a considerable accumulation of empirical data on behavior of atmospheric transparency for all

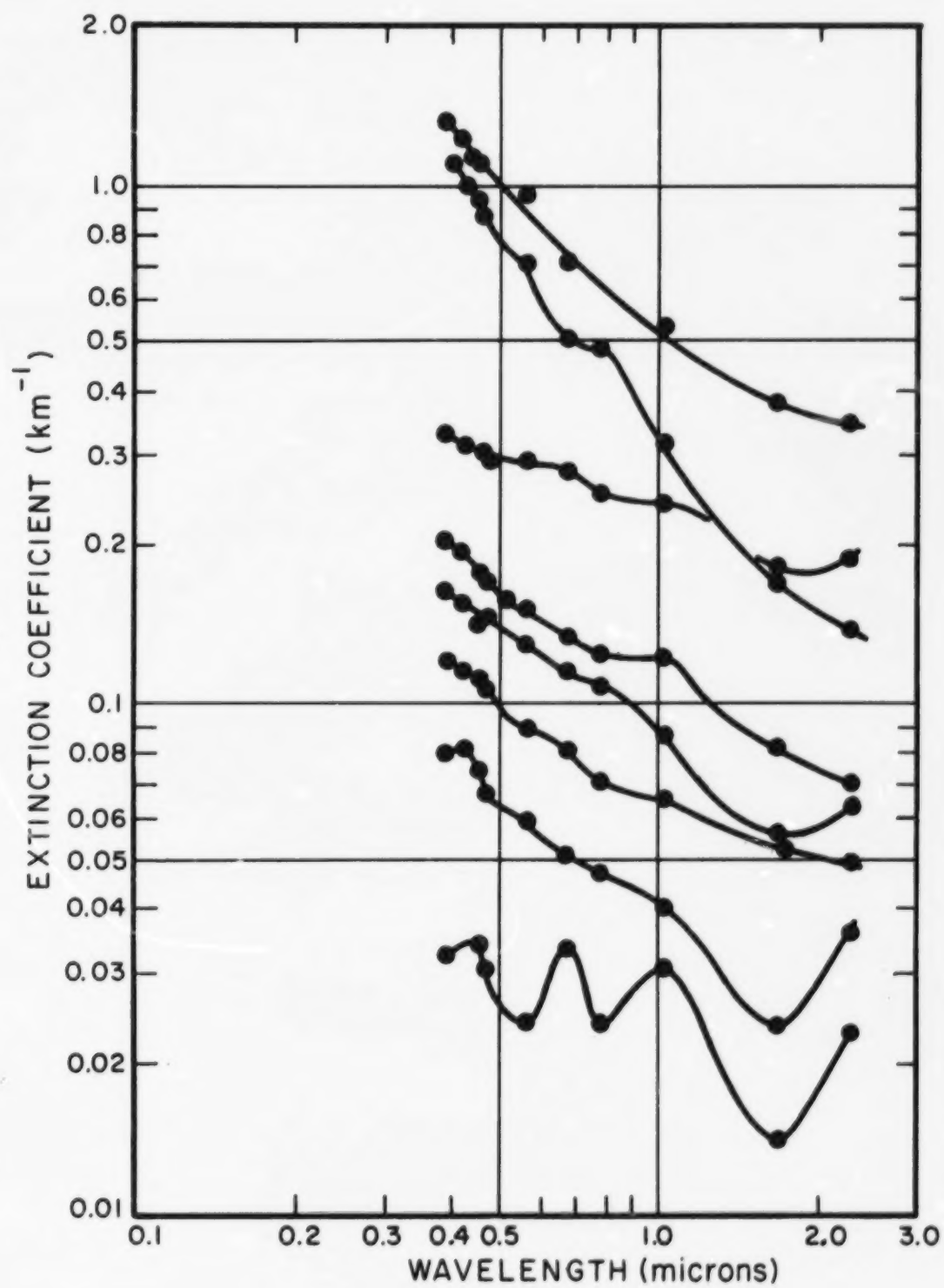


FIG. 12 SPECTRAL TRANSMISSION FOR VARIOUS AEROSOL DISTRIBUTIONS, AS MEASURED BY CURCIO [49].

sorts of meteorological conditions and mutual geometries of the source and the receiver. What can be said about the interpretation of these data? Unfortunately, this problem is still far from its solution. There have been several attempts to classify experimental results by the spectral behavior of atmospheric transparency [54,355] and in certain cases to approximate this behavior by a power law [126]. In a very much simplified picture of atmospheric attenuation (Bouguer's law with the total extinction coefficient being the sum of single-particle extinction coefficients, spherical scatterers), one can derive the power law for the spectral dependence of transparency from a power law for the aerosol size distribution curve [354,362].

This result is of little value however since its derivation does not allow for multiple scattering, partial coherence of individually scattered waves for small scattering angles [100,101], and general aerosol composition and size-distribution functions.

In this connection we must point out that the most popular way to describe visibility reduction in a turbid atmosphere in terms of Bouguer's laws ($I = I_0 e^{-\gamma L}$) is subject at present to severe criticism [273,384]. The latter is based on the fact that, in addition to direct light from the source, the receiver also takes up the light which results from the multiple scattering in the atmosphere. The relative role of the latter increases with the optical depth and the receiver's aperture.

According to Rozenberg [273], the deviations from Bouguer law in typical experimental situations reach the values of 10% when $\gamma L \sim 10$ and 100% when $\gamma L \sim 13$ (vertical transparency). Experimental determination of the limits of validity of this law for spatially limited light beams has been performed by Zuev, Kabanov, and Savel'ev [384], who have used a cloud chamber for water fogs,

and smoke and a lycopodium suspension in a solution of alcohol and water. In the latter case, the authors were dealing with a highly monodisperse hydrosol which permitted quantitatively reliable interpretation. The results of this investigations are summarized in Fig. 13; the ordinate gives the brightness of the light beam attenuated by the medium on a logarithmic scale and the abscissa gives the optical depth measured with photometers. One can see that the applicability of the exponential law is restricted to the range of optical depths up to $\gamma L \sim 12$.

Whether transparency measurements can be used to determine the aerosol content of the atmosphere is a question that has always intrigued atmospheric optics experts.

A method of particle sizing from spectral transparency measurements suggested by Shifrin *et al.* [299,300,301,302] was worked out essentially for 'soft' particles (with refractive index close to that of the surrounding medium). For the tabulated transparency, an approximate inversion formula for solving the integral equation

$$T(\lambda) = \int_0^{\infty} 2\pi r^2 \kappa(\lambda, r) n(r) dr \quad (15)$$

[r - particle's radius, $n(r)$ - size distribution, $\kappa(\lambda, r)$ - single particle attenuation cross-section, λ - wavelength of light, $T(\lambda)$ - total transparency] has been obtained. The inversion was shown to be possible when a sufficient amount of transparency data in the range of its essential variation, and asymptotic behavior of $T(\lambda)$ in the range of geometrical optics are known. However, the inversion formula of Shifrin and Perelman contains oscillating functions with the amplitude of oscillations increasing rapidly with the upper limit of the size spectrum and

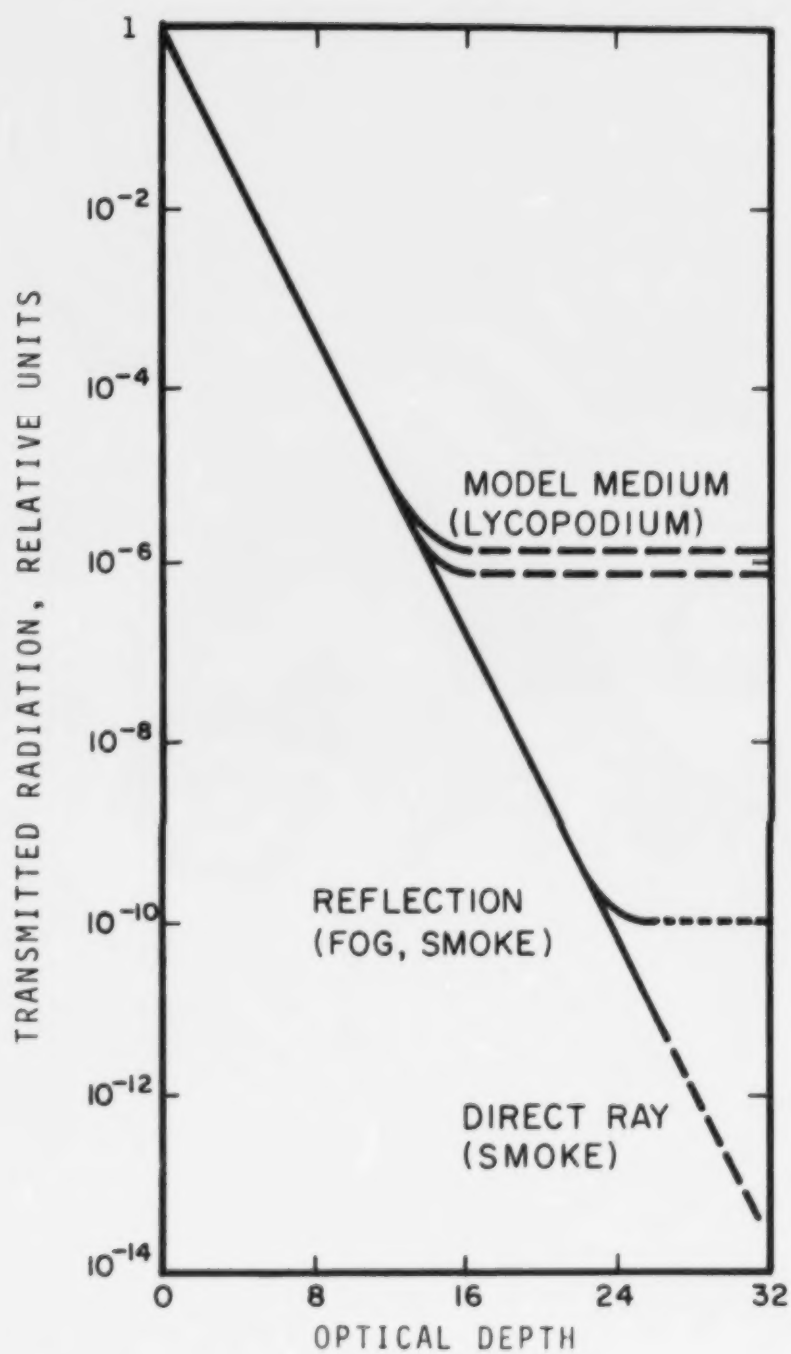


FIG. 13 LIMITS OF APPLICABILITY OF THE EXPONENTIAL LAW.

the upper frequency limit of transparency measurements. This, in turn, results in a rapid growth of errors as one considers wider size distributions; hence the obvious limitations of this method.

Experimental check of the Shifrin-Perelman transparency method was performed on two models [303]: (1) microcrystals of Ag Br in gelatine (particle radii about 0.3μ) and (2) spores of *Calvatia* (particle radius about 2.5μ). In both cases, dispersion of the size distribution was relatively small.

The fact that the authors have obtained satisfactory agreement when using large values of m^* ($m \sim 1.5$) and nonspherical particles points to serious limitations of the sensitivity of any transparency methods used for particle identification (see also [225]).

It appears clear that the transparency method alone is not sufficient to determine uniquely all the parameters specifying the aerosol structure. The method should be regarded rather as a source of additional information on the state of aerosol in atmosphere. If taken together with data obtained from other measurements, the transparency figures can then be helpful in obtaining a complete set of numbers characterizing a particular aerosol composition. If the parameters specifying the size distribution and total concentration in a chemically homogeneous aerosol system are known from independent experiments, the transparency method can provide the value of refractive index, i.e., identify the particles chemically.

Experiments with attenuation by artificial fogs [148,360] with controlled size distribution confirm this conclusion.

* m is refractive index of the particle relative to the medium.

B. Sky Luminance

Attempts to use the natural setting for scattering measurements which is provided by the distribution of sky brightness have a long history. First papers [142,261,362] contained a belief that the sky luminance is formed primarily by Rayleigh and aerosol single scattering, the aerosol being distributed in the lowest 3000 m of the atmosphere. Volz [362] has collected data on sky brightness for many days under various meteorological conditions. His measurements were performed for different wavelengths and included arrangements for various angular distances from the sun in the range from 0.2° to 120° . Analysis of the data obtained in these experiments has led Volz to a semiquantitative classification of the atmospheric conditions responsible for each type of brightness patterns. His classification was based on Mie calculations for aerosol sizes distributed according to a power law. Notwithstanding more than a doubtful question of the applicability of this model to real atmosphere, it is worthwhile to notice that Volz was among the first to stress the optical significance of the range of large particles (from 0.1 to 0.6μ).

The approach of Pyaskovskaya-Fesenkova [248,249,250] was aimed at obtaining information on the vertical distribution of the scattering function from the angular pattern of sky luminance. A separate role was assigned to the measurements in solar almucantar since, under the assumption of horizontal homogeneity of the atmosphere, these measurements were believed to be sufficient for determining the scattering function at any given solar zenith distance.

Other authors [156,341] studied the sky brightness in the aureole part of the sky. The measurements in solar aureols at various distances from the sun give data on the scattering

functions for small scattering angles, which are the most sensitive to the size distribution of the scattering particles [297]. At the same time, as it was shown in Ref. 156, the slope of the sky luminance in the solar aureole (expressed as a function of the angular distance from the sun) does not depend on the total concentration of the particles.

A theoretical interpretation of sky luminance data making use of single-scattering concept has been given by Bullrich [30] who considered a number of aerosol concentration and size distributions. On the other hand, a more consistent approach based on solution of radiation transport equation had been vigorously developed [9,29,46,78,102] both in the West and in the USSR. First fundamental treatment of the light transport in the atmosphere appeared in Refs. 6,39,204,313, and 316.

The physical argument behind the mathematical formalism of the transport equation is very simple: the change of the light intensity as the light passes through an elementary volume of a scattering medium is caused by losses due to extinction in this volume and by the light scattered inside the volume from other directions. Multiple scattering is thus taken into account through integration over the whole medium.

In its direct formulation the problem of radiative transfer can be stated as follows: given the average absorption and scattering characteristics of the medium together with the boundary conditions describing illumination regime and reflection from the ground, one has to find the distribution of light intensity as dependent on the angular and spatial coordinates. Exact analytical solution of this problem is possible only for simplest (and never-to-be-realized) angular shapes of scattering functions and for the Rayleigh atmosphere [29,46].

The presence of aerosol in the atmosphere causes considerable deformation of the scattering function with a tendency to form a large peak in forward direction. In the 1950's, there were developed so-called 'small angle approximation' methods [20,318] that enable one to determine solution of the transport equation in the case of elongated scattering functions with sufficient accuracy in the region of small angles. A further breakthrough came with the work of T.A. Germogenova [102], who suggested separation of the factor of the solution characterized by strong angular variation from a relatively smooth unknown function. Such separation becomes possible after a qualitative investigation of the solution of the transport equation or of the equivalent integral equation. The problem is then reduced to finding a slowly varying function which can be represented with sufficient accuracy by a lower-order Legendre polynomial; the approach to such problems had been previously developed [39,170,203].

The availability of fast modern computers has led to the formulation of efficient numerical methods for solving the radiation transport problem. The most widespread of these are Monte Carlo methods based on considering a random trajectory of a photon with certain probabilities of absorption and scattering.

A good up-to-date review of Monte Carlo techniques as applied to problems of atmospheric optics is presented in Ref. 202. Advantages of these techniques follow from the possibility of modeling the real physical processes by means of relatively simple algorithms. The mathematical model of the atmosphere can thus be constructed with maximal closeness to reality (e.g., nonuniform albedo, vertical distribution of aerosol, etc.).

All the effort described above was devoted essentially to solving the direct problem of radiation transport: on the basis

of known local properties of the medium, to find the angular and spectral distribution of radiation on a certain plain. The procedures, as one can see, are by no means trivial. On the other hand, determination of aerosol parameters from the distribution of sky luminance should follow from solution of the inverse radiation problem: by the spectral and angular dependence of radiation flux, to find the local optical parameters of the atmosphere. As far as we know, there has been no successful attempt to solve the inverse problem for an atmosphere model in any sense close to reality.

Recent scarce publications on sky luminance [90,276] contain at most hints of qualitative identification of aerosol particles responsible for a given intensity and polarization pattern.

C. Scattering by Atmospheric Aerosols

Perhaps the best written monographs explaining the physical aspects of light scattering by aerosols are those of Shifrin [297] and V. de Hulst [354]. The second of these adopts throughout a consistent mathematical formalism based on the concept of Stokes parameters for the light beam and their transformation during scattering described by the scattering matrix.

Stokes formalism. The unique advantage of Stokes parameters, first introduced in Ref. 325, is that they can adequately represent the state of partial polarization. They are defined as follows

$$\begin{aligned}
 S_1 &= \rho_{11} + \rho_{22} \\
 S_2 &= \rho_{11} - \rho_{22} \\
 S_3 &= 2\text{Re}\rho_{12} \\
 S_4 &= 2\text{Im}\rho_{12}
 \end{aligned}
 \tag{16}$$

where $\rho_{ik} = \langle E_i E_k^* \rangle$ is the density matrix of the scattered light [74,75,76]; E_i and E_k are the projection of the electric field vector on two mutually orthogonal directions; and the averaging is taken over an appropriate statistical ensemble of the radiation field. If a light wave is formed as an incoherent superposition of a set of waves, its Stokes parameters are sums of the respective Stokes parameters of the separate waves.

Experimentally observed quantities (the degree of polarization p , the ellipticity $\text{tg}\zeta$, and the orientation of polarization ellipse ψ) are related to Stokes parameters by means of simple algebraic formulae:

$$p = \frac{\sqrt{S_2^2 + S_3^2 + S_4^2}}{S_1} \tag{17}$$

†The degree of polarization as defined here means the ratio of the intensity of the completely (elliptically) polarized portion of the wave to the total intensity. This definition differs from an over-simplified one sometimes employed by field investigators:

$$p = \frac{I_{11} - I_1}{I_{11} + I_1} \tag{18}$$

$$\sin 2\zeta = \frac{S_4}{\sqrt{S_2^2 + S_3^2 + S_4^2}} \quad (19)$$

$$\operatorname{tg} 2\psi = \frac{S_3}{S_2} \quad (20)$$

If the incident and the scattered light beams are characterized by two sets of Stokes parameters $S_i^{(0)}$ and S_i , respectively, then the scattering process can be interpreted as that of transformation expressing S_i through $S_i^{(0)}$. It can be shown that this transformation is linear [272]. We thus come to the concept of the scattering matrix:

$$S_i = \frac{1}{k^2 R^2} F_{i\ell} S_\ell^{(0)} \quad (21)$$

where the factor $1/k^2 R^2$ describes the usual spatial attenuation of light in a spherical wave; $F_{i\ell}$ is a 16-component matrix which contains all the information on the optical properties of the scatterer. It is important that the elements of this matrix are completely independent of the properties of the incident beam; it is in terms of these elements, and not in terms of intensity and polarization characteristics of the scattered radiation, that any correct description of the scattering medium can be accomplished.

The light scattered by an aerosol containing volume in the atmosphere consists of the sum of waves scattered by each

where I_{11} and I_1 stand for the values of intensity of light polarized in two mutually normal directions. The incorrectness of Eq. 18 is most clearly demonstrated by complete circular polarization when $I_{11} = I_1$ and $p=0$.

particle. The question of statistical dependence of these waves ('coherent scattering') [101] arises when there is long range interaction between the particles* or when one considers scattering by small angles. The coherency of scattering in the latter case results from the fact that the phase shift in the light scattered forward depends very little on the position of the particle. Other situations in atmospheric optics can be regarded as those of statistically independent scattering; the elements of the scattering matrix in this case are additive.

Single-particle scattering. The problem of scattering by a *single particle* in atmospheric optics is thus of major importance. The simplest case of a homogeneous scattering sphere has been studied most extensively [213, 279, 354]. The mathematical formalism in this case consists of two Helmholtz-type equations for the inside and the outside regions together with the conjugation conditions at the boundary. The solution of this boundary value problem exists as an infinite series with respect to Legendre polynomials and their derivatives; the convergence of these series depends essentially on the value of parameter $\rho = 2\pi r/\lambda$ (r - particle radius, λ - the wavelength of the radiation). When $\rho \ll 1$ (the particle is much smaller than the wavelength), the first term of the series gives sufficient accuracy; the intensity distribution of the scattered light follows the well-known Rayleigh pattern:

$$I(\theta, \lambda) = I_0 \frac{9\pi^2 v^2}{\lambda^4 R^2} \left[\frac{m^2 - 1}{m^2 + 2} \right]^2 \frac{1 + \cos^2 \theta}{2} . \quad (22)$$

*For example, Coulomb interaction in electrically charged clouds.

Here I_0 is the intensity of the incident (unpolarized) radiation, v - the particle's volume, m - its refractive index.

Equation 22 describes a function which is symmetric in forward-backward directions; with the increase of ρ this symmetry gradually disappears. This effect manifests itself not only in the growth of the front lobe, but also in the appearance of other maxima leading to extremely complicated shapes (see Fig. 14).

Only a few years ago, tremendous efforts were made to develop various approximation methods [297,354] to calculate the intensity and polarization distributions for larger spherical particles in certain regions of their optical parameters; these methods were meant to make it possible to avoid the direct summation of the Mie series. Now with third-generation computers, most of these methods seem obsolete. Common practice today is to compute the angular functions and then discard them after they are used. A complete summary of published Mie computations up to 1963 exists in the report of Pendorf [234]. Among the recent publications on Mie scattering is that of Gucker *et al.* [115], which calculates angular intensity functions for the refractive index 1.486 over a wide range of sizes. These results presented in terms of intensity contour diagrams indicate the position of maxima and minima of angular intensities as a function of the particle size and the angle of observation. Twomey and Howell [347] have calculated the Mie intensities for fog and haze droplets. There are also unpublished materials [346] on scattering and extinction coefficients for complex refractive indices. The angular intensity distributions for visible light for water droplets as large as 1 mm in diameter were computed by Querfeld [251] with angular increments of 0.01° . The results of Mie calculations for aluminum oxide and magnesium oxide particles (the combustion products in solid propellant rockets) were published by Plas [241, 242].

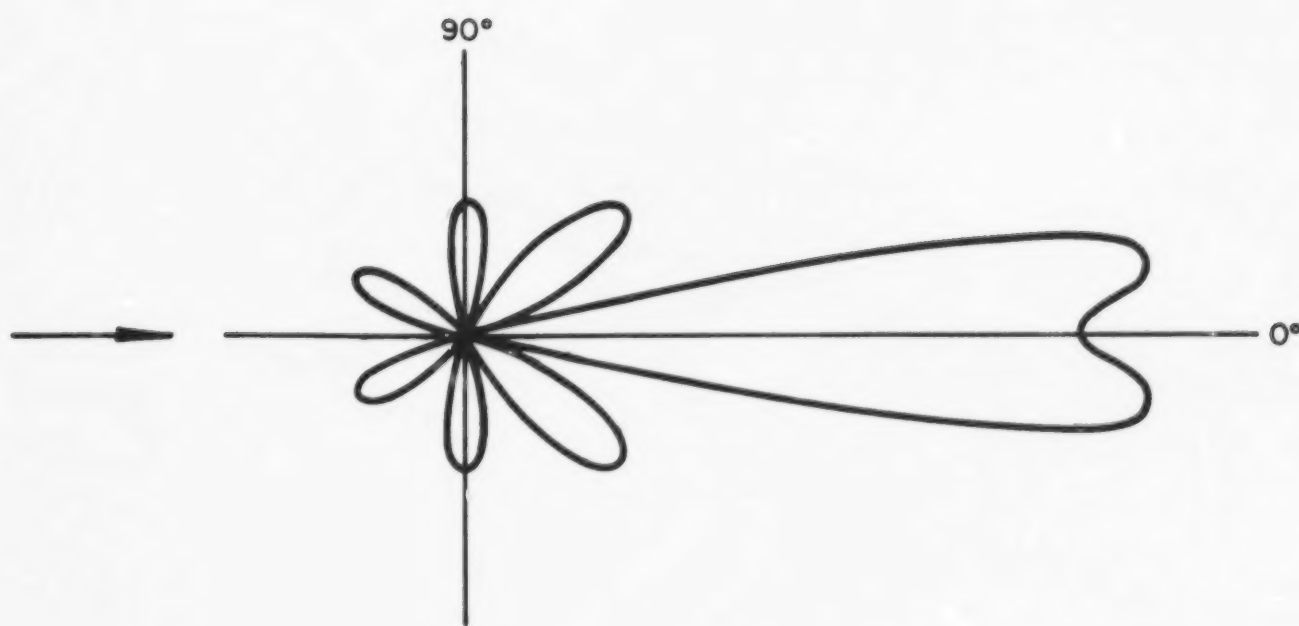


FIG.14 THE SCATTERING FUNCTION OF A
LARGE WEAKLY REFRACTING PARTICLE.

Scattering by nonspherical particles presents a much more difficult problem. The best studied body after the sphere is a homogeneous circular (infinite) cylinder. The problem of scattering by a homogeneous cylinder with arbitrary radius and refractive index in the case of normal incidence was first treated by Rayleigh [256,258]; other authors [289,363] have carried out numerical computations for various values of refractive index and the wavelength. Oblique incidence was analyzed in Refs. 31 and 366; the formulae for the scattered intensity in this case are much more complicated and there exist very few numerical results. A more recent paper [73] contains the scattering functions of infinitely long, hollow, coated cylinders at perpendicular incidence for several refractive indices and variable geometry of the scatterers. Yeh [380,381] and Burke *et al.* [32,33] have studied the case of elliptical cylinders at perpendicular and oblique incidence. Apparently the most difficult problem (for oblique incidence) is to obtain the formulae for the scattered radiation in the coordinate system associated with the incident wave. If in the far-field zone the scattered wave can be regarded as spherical, then its each component specified by a Legendre associate polynomial of a certain order is transformed during rotation of coordinate system according to a corresponding representation of rotation group [96]. This means that each l th-order term becomes a linear combination of $2l + 1$ similar expressions, which leads to considerable mathematical complexity of the problem.

The situation is somewhat brighter for particles which are small compared to the wavelength of radiation. When $\rho \ll 1$, the angular scattering pattern does not depend any longer on the particle shape: each body gives rise to Rayleigh scattering with polarizability (which determines only the absolute value of the scattered intensity) being a functional of the shape, size and refractive index of the particle [41,91,257,259].

A relatively simple solution also exists for the particles with weak refractive properties (the value of refractive index m is close to 1) and small phase shift across the particle ($2\pi|m-1| \ll 1$).^{*} In this case, it can be assumed that the effective electro-magnetic field inside the particle is the same as that in the incident wave; then each particle's element gives rise to a Rayleigh scattering and the resulting field is obtained as the sum of elementary waves. The angular distribution of the scattered radiation depends essentially on the particle's shape through the phase integral which sums up all the relative phase shifts between elementary waves.

This case is called Rayleigh-Gans scattering; its formalism was applied to spheres [92,256], including those with nonhomogeneous density distribution [77,354], ellipsoids [354], and circular cylinders [226,386]. Relatively less-known, but much more important, is the method suggested by Shifrin [294,295,296]. This method which has also been developed for bodies with optical properties close to those of the surrounding medium, contains the Rayleigh-Gans results as its first approximation.

Shifrin has reformulated the Mie boundary value problem in terms of an integral equation for the 'effective field' E_{eff} and applied an iteration procedure for solving this equation. The rate of convergence of the iteration series in this method depends on (but is not completely determined by) the value of the parameter

$$\alpha = \frac{3}{4\pi} \frac{m^2-1}{m^2+2} \quad (23)$$

^{*}In atmospheric optics this condition implies severe limitations on particles' size.

which is quite small for all the cases of practical interest in atmospheric optics (see Table X). Another important factor is the total dipole moment formed by all the molecules of the scatterer; this means a limitation on the particle's size.

TABLE X. Dielectric parameters of typical aerosols.

Dielectric Constant $\epsilon = m^2$	$\frac{\epsilon - 1}{4\pi}$	Conductivity	α
1.77 (water)	0.061	0	0.048
1.71 (ice)	0.056	0	0.045
1.56 (HCl)	0.044	0	0.037

Shifrin has analyzed the scattering by spheres in terms of the first and the second approximation of this method, and compared the results with exact Mie solution for $\rho=0.4$ and $\rho=0.8$. When $\rho=0.4$, the first approximation (Rayleigh-Gans formula) gives the error 5%; with the second approximation it becomes less than 0.8%. For larger spheres ($\rho=0.8$), the corresponding errors are 12% and 2%; the same accuracy in summation of the Mie series requires taking six terms into account.

Among the cases treated by Shifrin method are elongated and oblate ellipsoids of rotation, disks, and rods. Since in this case the particles may belong to the next size range after the Rayleigh and Rayleigh-Gans types, the role of the particle's shape becomes considerably more pronounced. (By comparison, as was mentioned before, the Rayleigh scattering is completely shape-independent.)

Figure 15 shows the angular distribution of the scattered intensity from an elongated ellipsoid of rotation with the long axis ten times greater than the short one; the direction of propagation of the incident light being transverse with respect to the long axis. The plane of the figure includes the wave vector of the incident wave and the long axis of the ellipsoid.

The importance of the Shifrin method is that it provides a relatively painless way to calculate the scattered field for non-spherical particles that are considerably larger than those of Rayleigh-Gans types, with limitations on material characteristics being satisfied in atmospheric aerosols.

When the wavelength of light is much smaller than the particle's size, the scattering process can be described in terms of geometrical optics [297,354]. The intensity distribution is obtained as a result of multiple reflections and refractions of light at the particle's surface. Nearly all light is scattered in the forward direction; its angular distribution is given by simple formulae containing Bessel functions.

There have been several proofs [133,297,355] of equivalency of the geometric optics treatment and the exact summation of Mie series for large spheres.

Polydisperse aerosol and optical methods of determining size distribution. The polydispersity of aerosols leads to a new optical problem: provided that the angular scattering pattern and the individual scattering functions are known, one has to find the size distribution of the aerosol system. To date, as far as we know, this problem has been formulated only for homogeneous polydisperse spheres. From the mathematical point of

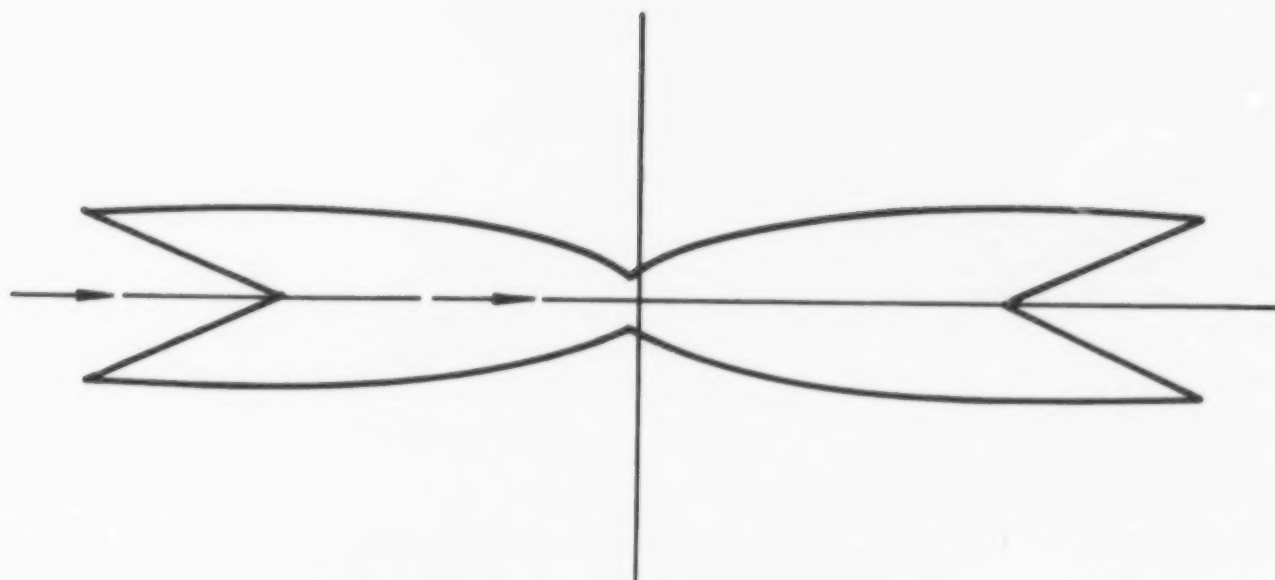


FIG. 15 THE SCATTERING FUNCTION OF A NONSPHERICAL PARTICLE.

view the problem is equivalent to the inversion of the integral equation:

$$I(\theta) = \int_0^{\infty} I_1(r, \theta) n(r) dr \quad (24)$$

where $I_1(r, \theta)$ is the single particle scattering function, $n(r)$ is the size distribution, and $I(\theta)$ is the scattering function of the total system, which is obtained in experiment. The single particle scattering function $I_1(r, \theta)$ is simply a solution of the Mie problem.

One way to approach Eq. 24 is to replace integration with a summation over finite-size intervals and to consider a system of algebraic equations formed by the algebraic equivalent of Eq. 24 at various angular points.

Unfortunately, as is the case with all Fredholm first-type equations, the resulting system is ill-conditioned; small errors in $I(\theta)$ produce large variations of $n(r)$. These difficulties necessitate the pursuit of a limited problem - to determine from the optical information only certain characteristics of the size distribution. In this sense, the models discussed in Chap. IV prove most useful.

Among the cases where an accurate inversion procedure leading to a full solution has been found is that of Rayleigh-Gans scattering [304]. The procedure for obtaining the solution of the integral equation was based on Mellin transformation. The authors have also obtained a formula for approximate calculation of the distribution function for a tabulated form of the total scattering function. It is essential that this formula contains only functions with limited amplitudes of oscillation which means that errors in the optical information do not result in

rapid growth of errors in solution. The way in which this formula operates was illustrated by an example of a Γ -distribution

$$n_{\mu}(r) \sim r^a e^{-br} . \quad (25)$$

Figure 16 shows successive approximations to the true curve (I) obtained with increasing values of the maximum scattering angle. The limits of the scattering angles ($\theta_{\min}$ and $\theta_{\max}$) determine the accuracy of the method.

An approach based on the use of models for size distributions was developed by Kolmakov [163]. He considered two- and three-parameter Γ -distributions for aerosol particles and limited his analysis to particle sizes much greater than the wavelength.

Special attention has been paid to the structure of the radiation field scattered at small angles [132,190,308]. As was shown by Hodkinson [132], for a spherical particle the angular distribution of light in the main lobe of a Fraunhofer diffraction pattern changes rapidly with its size but is relatively stable with respect to variations of refractive index. On the basis of available Mie theory computations for medium and large transparent and moderately-absorbing spheres (ρ varying from 0.1 to 150), Hodkinson argues convincingly that, even though the assumptions of large particle size and forward scattering are not valid over the above range of variation of the particle's radius, the shape of the forward lobe as given by the Fraunhofer diffraction formula reflects the true one remarkably well, even down to $\rho=1$ (see Fig. 17). The obliquity factor of the slope in the front lobe can thus provide a useful estimate of the particle's size.

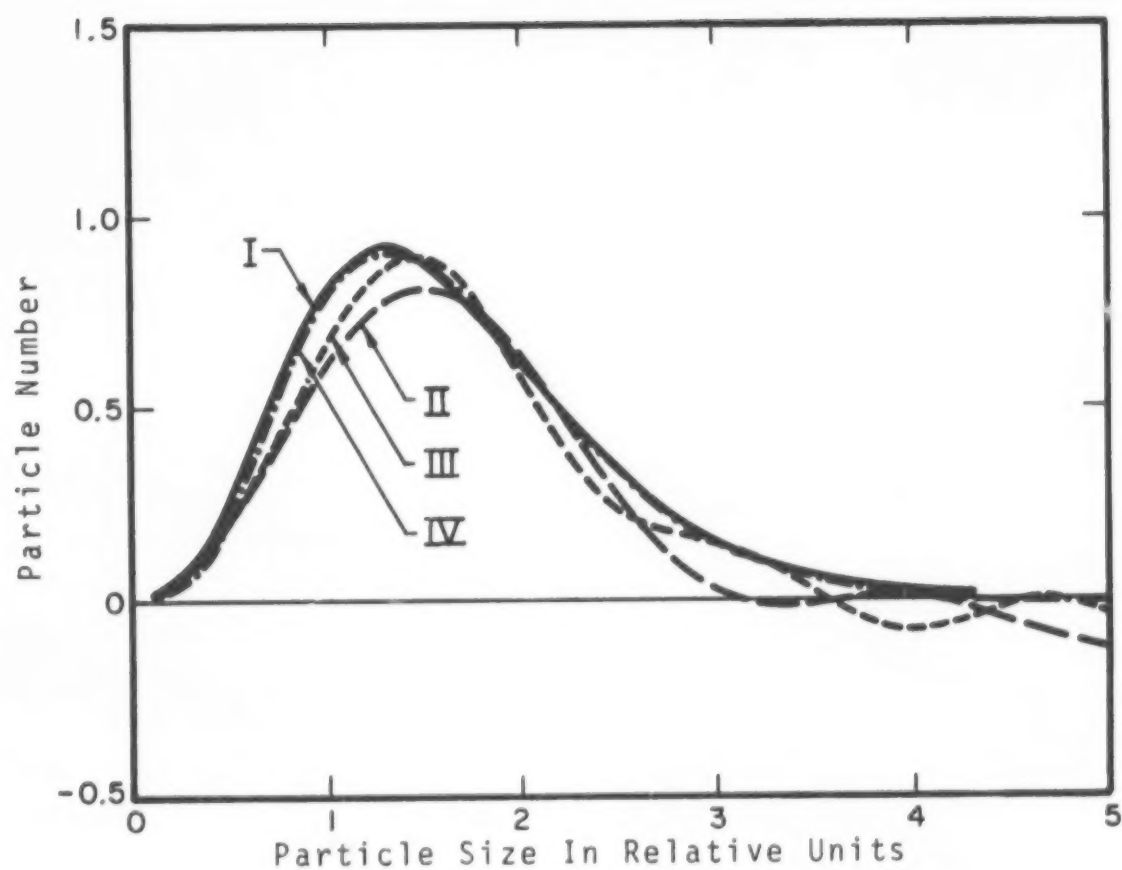


FIG.16 INVERSION OF THE SCATTERING PATTERN:
 I: THE EXACT CURVE
 II, III, IV: SUCCESSIVE APPROXIMATIONS.

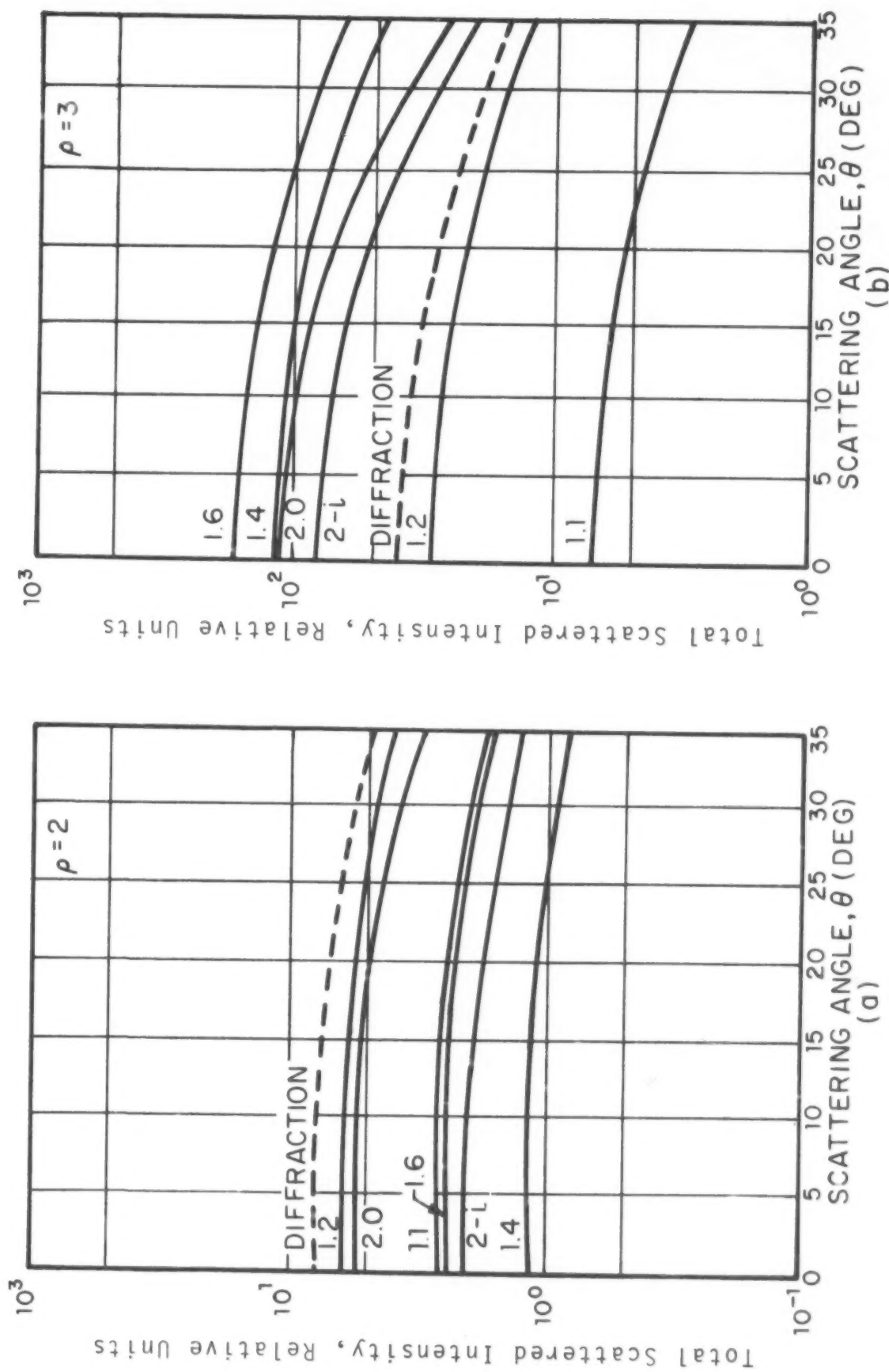


FIG. 17 ANGULAR VARIATION OF THE SCATTERING FUNCTION IN THE FORWARD LOBE FOR VARIOUS VALUES OF REFRACTIVE INDEX.

Shifrin, Perelman and Punina [307] performed detailed theoretical studies of the forward lobe for large spheres and calculated its shape for polydisperse systems with Γ -distribution. The results presented as tables were shown to be valid in the angular range which depends on size distribution parameters.

Similar calculations for Junge-type distributions were carried out by Toropova [342] and Toropova and Obasheva [343], who analyzed the cases of two different refractive indices and studied the effect of refractive index on the degree of symmetry of the scattering function.

In Ref. 308, the authors studied the shape of polydisperse scattering functions for generalized Junge distribution and 'soft' particles (Rayleigh-Gans scattering); the near forward scattering also proved to be the most important from the point of view of sensitivity to the variations of the size distribution parameter (see also, Ref. 253).

On the basis of information thus obtained, several authors [164, 298, 306] suggested a method for determining the size distribution from small angle scattering.

The inversion problem was modeled [164] on an analog computer and the procedure was shown to provide an accurate solution for small sizes at high operating speed.

A most detailed study of a polydisperse system of *non-spherical* particles has been recently performed by Holland and Draper [139]; the authors were dealing with randomly oriented disks with irregular edges. The polar nephelometer, which essentially consisted of a horizontal light-beam illuminating a cloud of particles with a photomultiplier photometer mounted on a rotating arm, allowed measurement of the angular distribution

of the intensity of light scattered by the cloud. Calibration of the optical system was achieved by comparing the scattered intensity with that reflected by a plane, diffuse reflector of known reflectance.

Comparison of experimental results with those calculated for an equivalent system of spherical particles shows that the scattering into the forward hemisphere is relatively nonsensitive to the particle's shape, whereas for the backscattering (at the angles larger than 120°) the discrepancy becomes quite pronounced.* The data of Holland and Draper demonstrates again the necessity of development of an adequate theory for scattering by non-spherical particles.

Another significant source of literature on scattering by polydisperse system is research in colloidal chemistry. The authors of Ref. 111 studied polymer latexes and oil-in-water emulsions by a small-angle method described in Ref. 190; quasi-monodisperse systems were studied by Johnston [149] and by Espenscheid *et al.* [71]; scattering by inhomogeneous spheres forming a polydisperse medium was analyzed in Ref. 72.

D. Polarization of Scattered Light

As was pointed out in the beginning of this Section, the only adequate characteristic of the optical properties of hazes

*A similar result was obtained by G.J. Gorchakov [107] in polarization measurements of the scattering matrix at dry atmospheric aerosols; the difference between the first and the second diagonal components at large scattering angles amounts to 5%-30%. (See also page 110.)

is the scattering matrix. Determination of the latter implies sufficiently refined polarization measurements. In recent years, this direction has been extensively pursued [61,68,107,108,109] and a series of important results for real atmospheric conditions has been obtained.

For a system of spherical particles, the scattering matrix exhibits a very high degree of symmetry:

$$F_{1\ell} = \begin{vmatrix} F_{11} & F_{12} & 0 & 0 \\ F_{12} & F_{11} & 0 & 0 \\ 0 & 0 & F_{33} & F_{34} \\ 0 & 0 & -F_{34} & F_{33} \end{vmatrix} \quad (26)$$

In the right-hand side of this expression there are only four independent parameters, instead of sixteen in a general case. From a physical point of view, the element F_{11} corresponds to the ordinary scattering function; normalized F_{12} gives the degree of linear polarization of the scattered light when the incident wave is nonpolarized; normalized F_{34} is the degree of ellipticity of polarization in the scattered light for the linear (diagonal) polarization of the incident wave; F_{33} gives the angle of orientation of the polarization ellipse.

Gorchakov [107] reports the results of the measurements of the scattering matrix carried out during the nights of October–November, 1963 and September–December, 1964. The material accumulated during 65 nights of measurements contains over 500 angular

functions for various illumination conditions. The relative humidity was varying in the interval 48%-100%.

A pronounced correlation was observed between the values of the scattering coefficient σ (the turbidity) of the air and the type of symmetry of the scattering matrix. For high values of turbidity, the scattering was shown to occur on spherical particles (with the scattering matrix being symmetric in the sense [26]). On the other hand, in hazes with $\gamma \leq 0.5 \div 2 \text{ km}^{-1}$ the component F_{22} differs from F_{11} the difference amounting to 5%-30% for large scattering angles. This should be regarded as the evidence of the presence of essentially anisotropic particles in dry hazes.

The above analysis shows that the magnitude of large angle scattering can be a sensitive indicator of the presence of non-spherical particles.

Figures 18 and 19 present results of Gorchakov in terms of the normalized scattering function and the degree of linear polarization of the scattered light for four different types of 'optical wather': haze, dense haze, fog, and drizzle. With the increase of the optical density, the scattering pattern acquires specific features of scattering by large particles. The maximum in F_{12} gradually moves towards 140° (rainbow angle) and is accompanied by formation of a maximum in F_{11} in the same angular region. This is a direct indication that the increase of the optical density of a haze is due mainly to condensation processes (see also, Chap. III). Essentially the same results (in terms of optical weather classification) were reported by Driving, Mikhailin and Rozenberg [61], who also measured the F_{12} component of the scattering matrix.

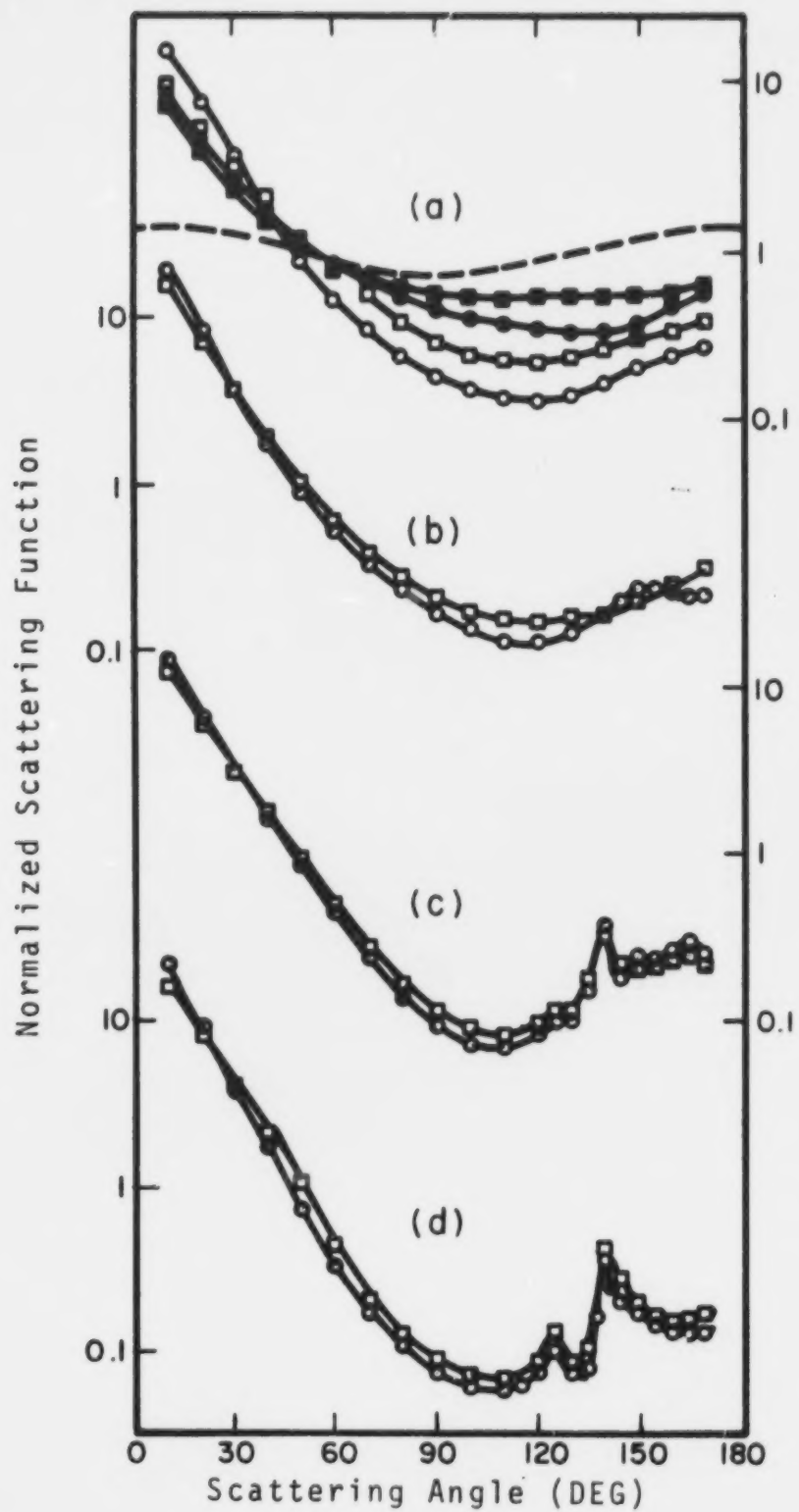


FIG.18 TYPICAL ANGULAR DISTRIBUTIONS OF THE NORMALIZED SCATTERING FUNCTION FOR (a) HAZE, (b) DENSE HAZE, (c) FOG, AND (d) DRIZZLE.

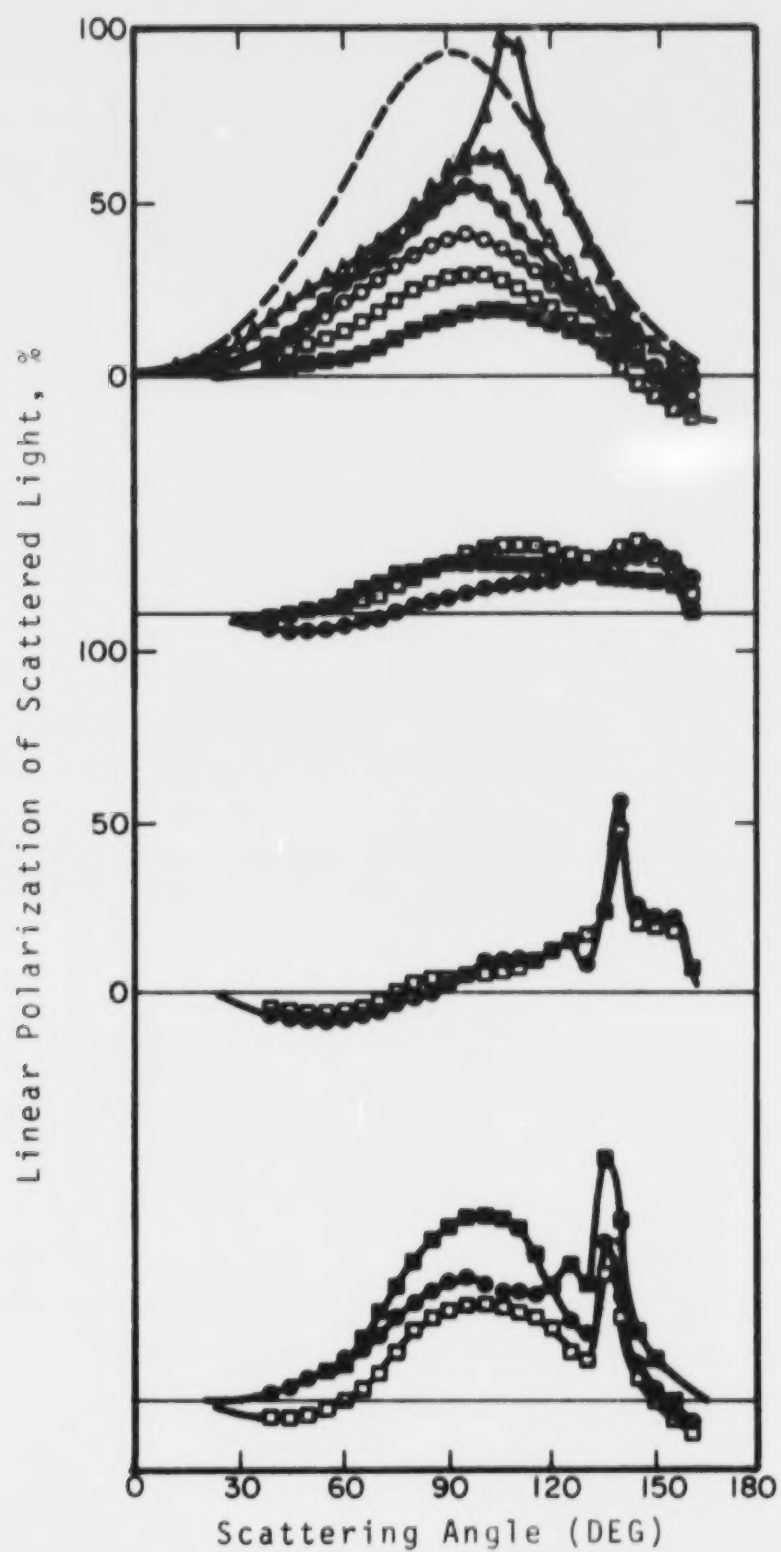


FIG.19 TYPICAL ANGULAR DEPENDENCE OF THE
NORMALIZED ELEMENT F_{21} ($F_{21} = -p$
WHERE p IS THE DEGREE OF LINEAR
POLARIZATION OF THE SCATTERED LIGHT).

Rozenberg [271] has summarized all recent polarization measurements in the atmosphere both in the USSR and in the West. The data on the correlation of the scattered intensity for various spectral intervals (see Table XI) indicate that the regularities governing the transition to heavier haze may be due to a certain dynamics of the size distribution of the haze particles. It is possible that the total number of the particles remains constant whereas their dimensions increase in a regular manner. This increase results in the formation of a qualitatively different system - dense haze with substantial fraction of large and giant particles with radii 1-5 μ and 12-15 μ . (By comparison, the average radius of particles in haze is $\sim .25\mu$).

TABLE XI. Normalized correlation matrix for the scattering coefficient in various spectral intervals.

λ, μ	0.38	0.40	0.45	0.50	0.55	0.60	0.68	0.74	0.80	1.0
0.38	1	0.968	0.950	0.912	0.886	0.882	0.876	0.853	0.852	0.747
0.40		1	0.949	0.871	0.846	0.853	0.864	0.836	0.839	0.724
0.45			1	0.943	0.931	0.927	0.931	0.900	0.888	0.774
0.50				1	0.972	0.952	0.914	0.915	0.885	0.781
0.55					1	0.972	0.924	0.917	0.903	0.783
0.60						1	0.941	0.920	0.910	0.786
0.68							1	0.965	0.920	0.803
0.74								1	0.922	0.826
0.80									1	0.804
1.00										1

The fraction in the 1-5 μ interval is responsible for rainbows; the giant particles determine the aureol part of the scattering function. As the dense haze changes its density, the effective radii of both fractions vary in the above limits, which can be traced by the displacement of rainbows and haloes.

E. Recommendations

1. The problem of immediate importance in the field of optical properties of air pollutants is to establish the correspondence between a certain set of optical parameters (appropriate combination of the elements of the scattering matrix) and the results of direct physico-chemical measurements for various types of hazes. This can be done along the lines suggested, for example, by Gorchakov and Rozenberg (see pp. 116-120). Then it will be possible to formulate specifications for creating a system for continuously monitoring the "pollution potential" of the atmosphere by optical means.
2. Since virtually nothing is known about the portion of dry aerosol which acts as condensation nuclei, techniques must be developed to allow discrimination between spherical and nonspherical particles. These techniques should be based on the solution of the problem of light scattering by a nonspherical particle of arbitrary size and shape.
3. In the field of polarization measurements, improvement of existing methods of obtaining the Stokes parameters is highly desirable. The goal should be the increase of accuracy by the reduction of both optical and electronic types of noise.

VII. INSTRUMENTATION TECHNIQUES FOR MEASURING HAZES

A. Optical Instrumentation

The physical background for aerosol-measuring devices based on optical principles follows from the preceding Chapter on the optical properties of aerosols. Accordingly, one can classify instrumentation into the following groups:

1. Devices for measuring the spectral transmission;
2. Instruments performing measurement of the scattered radiation (photometers, monochromators, nephelometers, Stokes polarimeters);
3. Remote sensors;
4. Single-particle counters;
5. Fog disdrometers based on laser holography.

The first group of this classification scheme does not contain anything unique from the optical point of view. A collimated beam and a suitable telephotometer with a series of filters are sufficient for carrying out most of the transmission measurements. As was already pointed out, the most severe limitations of this technique follow from the ambiguities in interpretation of any transmission measurement.

Development of equipment for measuring the angular distribution of the scattered intensity has been very fast. Integrating nephelometers [21,275] which give the total scattered flux (with compensation in forward and backward directions) are used for extinction measurements in order to avoid extremely long geometrical distances.

Among the instruments in use are the Forward Scattering Smoke Photometer [388], a comparison photometer developed by Gucker and Peterson, the Sinclair-Phoenix Aerosol Photometer, etc. A typical schematic diagram of a photometer based on the forward scattering technique is presented on Fig. 20. Other small-angle scattering instruments were developed by Plaza *et al.* [244], Beebe and Marchessault [13], and Keijzers *et al.* [160]. The statement of the manufacturers* - that the forward scattering reading gives the logarithm of the mass concentration of the particles, when the physical characteristics of the latter (presumably, composition, size and shape distribution and refractive index) remain constant - is very difficult to prove. One either must perform theoretical calculations of the forward scattering intensity for various polydisperse systems of general composition, or calibrate the instrument for all possible distributions. Neither of these procedures seems feasible at present.

Instruments that give angular scan of the scattered light [174, 310] can, in principle, provide much more information on aerosol composition; they are particularly useful for monodisperse systems. In this case simple counting of the maxima in higher-order Tyndall spectra will give the particle size with relatively high accuracy.

Instruments for angular scattering are also built with laser light sources [27, 95, 369]; for visible light [205], as well as for ultraviolet [103].

The next generation of instruments measuring the angular distribution of the scattered light includes Stokes-polarimeters [14, 107, 121, 144, 245, 291]. The device developed by Gorchakov [107] consists of a Sekera polarimeter in combination with the registration principle suggested in Ref. 14 (see Fig. 21). Selection of various

*Phoenix Precision Instrument Co.

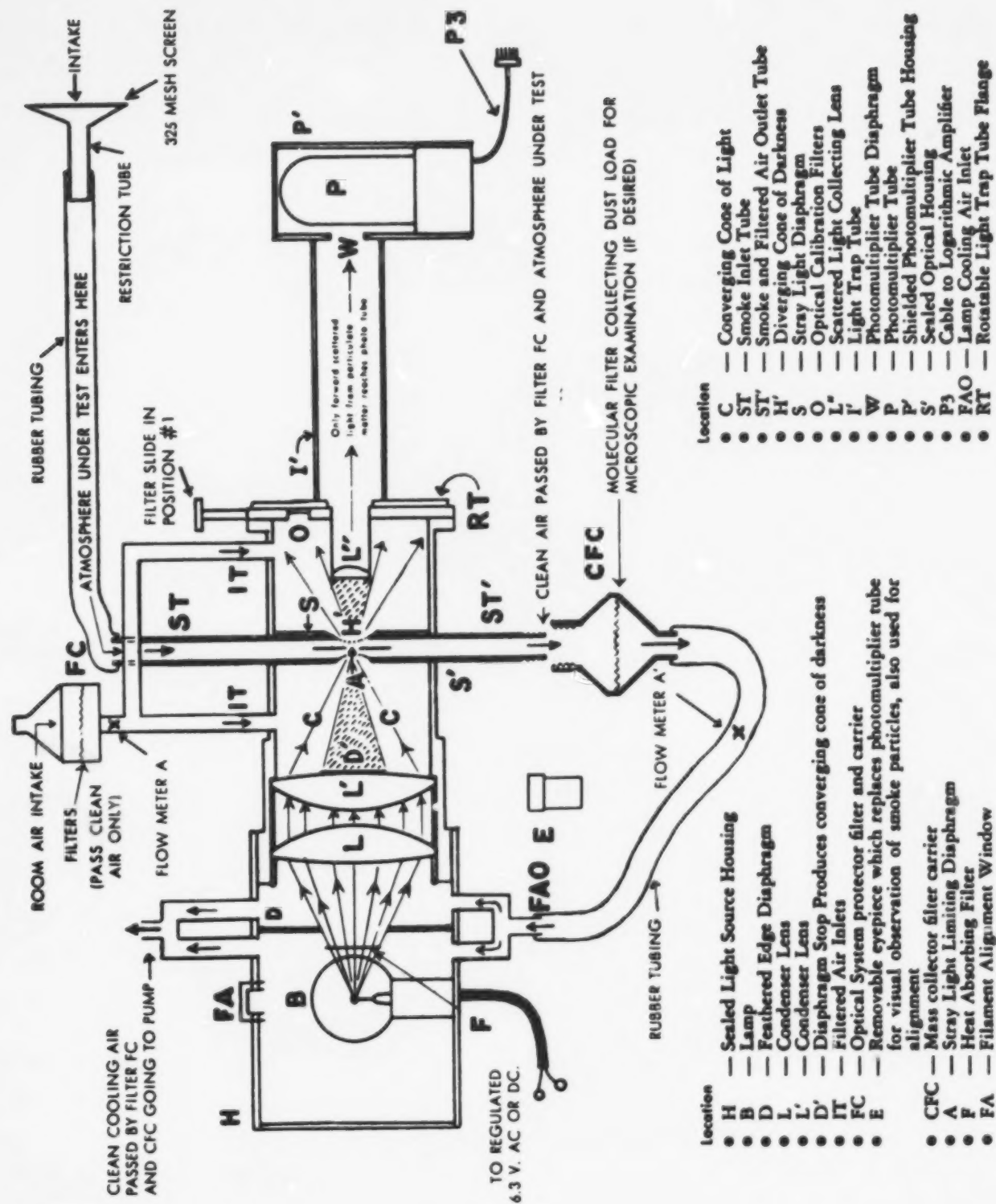


FIG. 20 SCHEMATIC DIAGRAM OF SINCLAIR-PHOENIX AEROSOL PHOTOMETER.

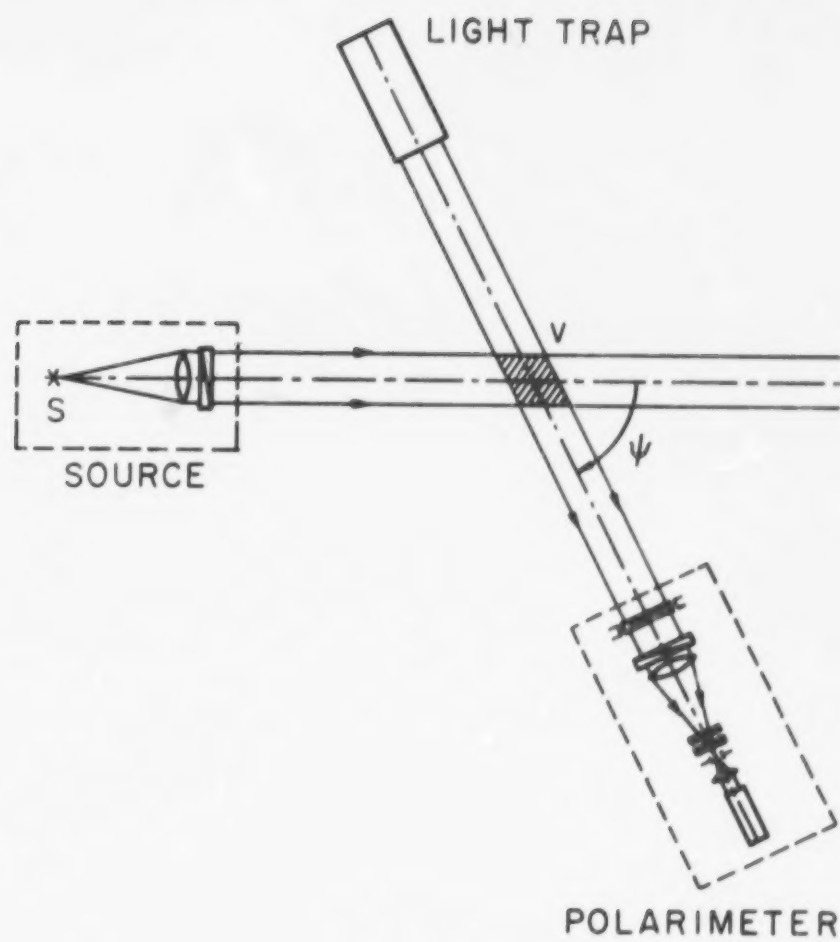


FIG.21 THE OPTICAL SCHEME OF THE STOKES POLARIMETER.

components of the Stokes vector is achieved by a modulator and a compensator. The circuitry is designed to register $S_1^i + (1 + \cos \tau/2) S_2^i, S_3^i, S_4^i$, where S_i^i are the components of the Stokes vector for the scattered light; τ is the phase shift of the compensator. The errors introduced by the optical part of the system are negligibly small; the main source of noise (1%-2%) is the circuitry.

Another very recent trend in optical instrumentation for measuring hazes is the application of remote sensors [196]. These can be used on satellites as well as on aircraft and balloons. Their obvious advantage is to be able to provide information on large-scale patterns of air pollution. The possibility to infer the aerosol content from the intensity and polarization of radiation as seen from a satellite was investigated by Plass and Kattawar [158,243], who applied the Monte Carlo method for calculating the effects of both Rayleigh and Mie scattering for a Lambertian earth surface. The difficulties in interpretation here are similar to those in the sky light intensity and polarization methods.

Among the instruments suggested for satellite use are filter-wheel radiometers, polychromator-radiometers, scanning spectrometers, interferometers, and optical correlation instruments. The present state of the art (mainly with respect to radiation transport theory) is such that only detection and not the quantitative analysis of aerosol layers is possible.

Probably the most fascinating and promising technique among those recently developed is that of single particle counting (see also Chap. IV). The principle behind this technique is that the particle cloud is sampled through a narrow light beam so that a pulse of light is registered at some angle when a particle enters the illumination field.

The single counting technique opens extremely broad possibilities for aerosol research. Not only average particle number in each size range but also higher-order moments (e.g., correlation functions between various sizes) can, in principle, be measured. At present there are single-particle counters with both fixed and variable scattering angles. Reliability of their performance depends on the homogeneity of chemical composition of the aerosol system; another serious limitation is the spherical shape of the particles.

Experimental and theoretical evaluation of the performance characteristics of single-particle counters can be found in Refs. 134, and 376.

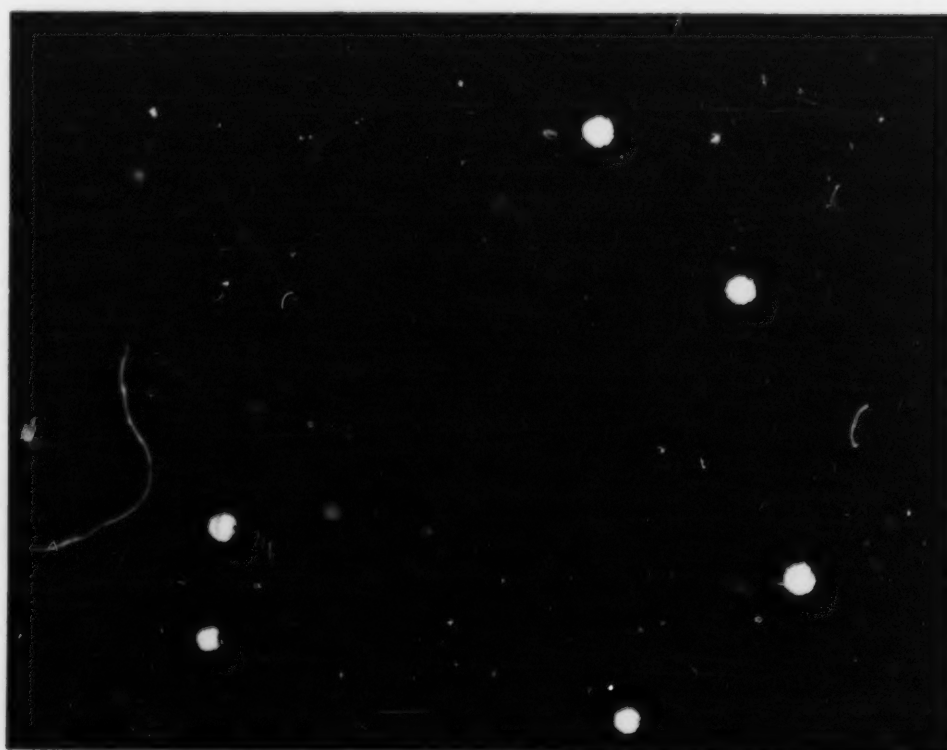
Laser holography provides another direct approach to optical measurements of haze particles. The physical principles of a 'Laser Fog Disdrometer' are discussed in Refs. 309, 334, 335, 336, 337, 338, 339, and 340 and can be formulated as diffraction effects produced by particles when illuminated by a coherent collimated quasi-monochromatic light beam. Because of the high speed of the particles in fogs it is necessary to have a very short exposure time and a high pulse-repetition frequency. A modern ruby laser with the wavelength 6943Å is capable of producing 1-2 microseconds pulses at repetition rates of about 10 c/min.

Silverman [309] suggests two different optical schemes: the spatial filtering and the coherent background method. Figure 22 presents typical recordings of glass beads of known sizes and water droplets obtained by the spatial filtering method.

The diffraction rings that appear on any hologram reconstruction image limit the degree of accuracy of the particle sizing; this limitation is essentially that of geometrical optics requirements.



(a)



(b)

FIG. 22 HOLOGRAM RECONSTRUCTION IMAGES OF GLASS BEADS AND WATER DROPLETS OBTAINED BY SPATIAL FILTERING METHOD.

B. Direct Sampling Methods

Devices for sampling particulates may be roughly categorized into instruments which simply collect material and instruments which collect and evaluate. Simple collecting devices must be brought back to the laboratory for evaluation after sampling but instruments that evaluate and may or may not collect the aerosol during sampling give some type of readout related to particle size, concentration, mass, etc.

Collection devices. One of the most common methods of particle collection is filtration. Particulate-laden air is drawn at a known volume through the filter media, where it is collected at some efficiency. The dust-laden filters are then sent to the laboratory for analysis by light transmission, weight, chemical analysis, or some form of microscopy. The type of filter media may vary according to the sampling and/or evaluation technique. Cellulose fiber media is commonly used for light transmission measurement; glass fiber or cellulose fiber are employed for mass measurements by weight or chemical analysis; resin base membrane media are used for microscopy. Sizes and shapes of filters vary according to the particular application. Jutze [153] recommends a certain method for sampling fine particulate matter. A composite filter developed by Harris [123] overcomes the problem of dust blown off of membrane filters; the filter is conventional membrane combined with a layer of flexible plastic foam.

The use of filtration is well adapted to mass sampling of particulates in a wide range of particle sizes from submicron to ≥ 50 microns. For haze studies, high-volume filtration may be employed to determine particulate loadings. This method is simple and well-defined by past experience.

Inertial separators [55] are widely-used devices for collecting medium-sized and coarse particulates. A separator imparts a diverting force to the particle to be removed from the carrier gas stream. This force is produced by directing the gas in a circular path or by effecting an abrupt change in direction. A cyclone separates particulate matter from carrier gas by transforming the velocity of the inlet stream into a double vortex confined within the cyclone. In the double vortex, the entering gas spirals downward at the outside and spirals upward at the inside of the cyclone outlet. The particulates, because of their inertia, tend to move toward the outside wall, from which they are led to a receiver. Petroll [239] tests and rates four different makes of small cyclones. Harris [122] describes a device called the "Simpeds" which is a portable battery-operated gravimetric airborne-dust sampler. It samples at 1.85 liters/min, uses a cyclone elutriator to separate coarse dust, and collects the fine airborne dust on a membrane filter for subsequent weighing and analysis.

Air centrifuges used for air sampling [3] include the conifuge, conicycle, and Goetz Aerosol Spectrometer. The conifuge is an air centrifuge formed by two concentric cones separated by a narrow annular space through which the aerosol is drawn at a rate of 25 ml/min. Particles are impacted on the inner surface of the outer cone, according to the aerodynamic size, with the largest particles at the top and the smaller particles toward the bottom.

The conicycle is a self-contained sampler consisting of a battery-pack, motor, and sampling head. The head is a cylindrical structure that rotates at 8000 rev/min and performs four functions: pumping air through itself at 10 liters/min; preventing particles above a predetermined Stokes diameter from entering the sampler; completely retaining all those particles entering the sampler that have a Stokes diameter greater than a smaller, predetermined value

(1 micron); and allowing particles below the lower limit of complete collection to pass through the sampler to an extent inversely proportional to their Stokes diameter. Inertial separators, in general, are not recommended for collection of particles less than 15 microns, but are quite useful as preseparators for other collectors when large particles are present. The cyclone could be used as a precollector in front of a high-efficiency filter (in order to extend the operating life of the filter). This procedure would be quite useful if the haze being sampled consists of a high fraction of large particles.

The Konimeter [3] a single stage impactor, is useful as a cutoff device for some other collecting method or for an experiment in which a maximum particle size is desired. The Sartorius version of the Konimeter consists of a tapered nozzle through which a stream of outside air is drawn by a small, spring-loaded pump to impinge near the perimeter of a circular glass plate. The plate can be rotated to receive up to 36 samples. The dust is deposited toward the center, so this instrument is of no use for particle size analysis but can be very useful for counting the number of particles in a given sample. The Konimeter is a fairly useful tool for making rapid evaluation of particle sizes. The measurements are not as accurate as those obtained by other particle sizing methods, but this instrument may be used for obtaining quick rough estimates so that more sophisticated instruments may be chosen with some degree of accuracy.

The cascade impactor was developed to overcome the disadvantages inherent with single stage impactors. This instrument has at least four impaction slits or nozzles of decreasing width, connected in series and mounted at decreasing distances above the collecting plates. Thus, the largest particles are collected on the first plate and the finest on the last and the overall dust sample

is divided into multiple size fractions. Conner [43] describes an inertial collector that employs essentially the same principle as a cascade impactor, however, deposition is on filters. The collector is a two-stage device operating at a flow rate of 1.4 cubic feet per minute. The particle size cut of the sampler is for a diameter of 1.4 microns. Separation of greater than 90 percent is obtained for particles below 0.8 microns and above 2.0 microns. Goetz [105] has modified a moving slide impactor for air pollution studies so that submicron aerosols (diameter ≥ 0.2 micron) may be collected. One advantage of this design over other particle classification devices is the availability of a uniform sample area large enough to permit repeated micro-optical evaluation at different locations of the same density level, thereby minimizing statistical fluctuation. A four-stage, high-flow rate impactor has been built by Lundgren [199] for the determination of aerosol concentration as a function of both particle size and time. The unit may be used in very dusty atmospheres for long sampling intervals (24 hr). The gas-borne particulate matter is collected on four rotating drums, each with a collection surface area of about 10 square inches. The rotating drums allow large quantities of material to be collected without particle buildup or blow-off. Mammarella [201] used a differential sampler with five elements in the form of a parallel piped with units which are superimposable and interchangeable as a four-stage sampler. Some variation of a cascade impactor is essential where particle-size data are required. Most impactors are limited in that the range of particle sizes collected is between 1-10 microns and the collection plates of the cascade impactor must be analyzed in the laboratory.

The Greenburg-Smith impinger [3] was the first sampling instrument of its type. It has a 2.3 mm bore and, at the standard flow rate of 28.3 liters/min, a jet velocity of 100 meters/sec and an

inlet suction of 3 inches of Mercury. The collecting efficiency is low for particles smaller than 0.7 micron but can be improved by operation at sonic velocity.

The Midget Impinger [3] is a smaller version of the Greenburg-Smith. It has a 1 mm bore and, at a standard flow of 2.83 liters/min, a jet velocity of 70 meters/sec and an inlet suction of 12 inches of water. Lynch [189] has replaced the standard ring seal of the midget impinger with an "O" ring joint to support the impinger tube in the head, thus alleviating the breakage problem. This also permits lateral adjustment of the orifice to the impinging surface. May [207] has developed a multistage impinger capable of attaining flow rates of 55 liters/min. Rates of evaporation and freezing are low and the impingement is gentle, since velocity does not reach sonic. The impinger is employed satisfactorily as a sampler where chemical analysis of the collected material is required. A suitable solvent may be used in the impinger to act as the collection medium, thus eliminating the additional step of dissolving the collected matter from filters in the laboratory.

The Rotorod Sampler [3] is an aerosol sampling device capable of collecting particles one micron in diameter and larger. It is powered by a standard 12-volt dry cell and is therefore well-suited for field and balloon-borne operation. The Rotorod sampler employs a principle not found previously in particle samplers. The collector, a thin U-shaped or H-shaped rod, is drawn through the aerosol-laden air. A compact constant-speed motor drives the coated collector rod through the air. Particles are impacted on the collector rod for subsequent inspection under a microscope. Rotorod samplers may prove adaptable for sampling haze since they are inexpensive and readily portable. Many of these devices can be spread out over a wide area to sample particles for latter microscope inspection. Rotorods, however, are not very good quantitative collectors

and must be used solely for particle size and not particle concentration analysis.

Electrostatic precipitators [3] separate the particles from the carrier gas by electrical rather than mechanical energy. Little electrical energy is required in the process since force is only applied to the particles and not the entire gas volume. Conventional electrostatic samplers are used when it is necessary to collect moderate-sized samples with high collection efficiency for all particle sizes. A high-volume electrostatic precipitator [191] that operates at 27 cfm collects samples on a single tube, 1-3/8 inches in diameter and 12 inches long. The sampler can be used with a cyclone or elutriator precollector, thus simulating upper respiratory retention for two-stage sampling without a significant reduction in sampling rate. Shale [292] has used a pilot-scale electrostatic precipitator operable at temperatures between 80°-1500°F and pressures of 35-80 psig using 3-inch electrode spacing. In conjunction with a cyclone or elutriator, the high volume electrostatic precipitation may be used quite readily for large volume haze sampling.

Thermal precipitators [3] deposit dust particles from a small volume of air onto a glass slide, where they can be examined, counted, and sized by microscope. Deposition is accomplished by the thermophoresis force experienced by an airborne particle in a temperature gradient. Velocities (and therefore flow rates) through the device must be small and therefore the principle application of the device is to the sampling of submicron aerosols. This sampler is best used when collecting haze samples for later analysis by electron microscopy.

The diffusion battery is a series of fine tubes or parallel flat plates that will remove particles from a flowing air stream with an efficiency dependent upon the particle's diffusional

mobility [89,348]. By operating the battery in accordance with the method of Fuchs [89], it is possible to determine the median diameter and standard geometric deviation of a submicron aerosol distribution.

Rich [263] has used a diffusion box with insulated plates to determine diffusion loss when the plates are at the same potential. With a few hundred volts applied, the device acts like a conventional diffusion box in series with a second device to remove charged particles. The diffusion battery is not generally used for haze measurement but is basically a simple tool and should prove most useful.

Collection and/or evaluation instruments. The sequential paper-tape air sampler [3] automatically draws air through a paper tape that is moved at preset intervals to expose a new sampling area. An adjustable timing device controls the length of time sampled on each spot; then, by photoelectrically monitoring the density of the spot, the relative contamination level is determined. A strip chart recorder collects this information as a permanent record.

Benarie [15] used a Prometheum¹⁴⁷ source in place of a photoelectric cell to detect the strain.

The TMII [86] employs a moving membrane tape to sample air at 80 cc/min. The concentration on the tape is read by reflectance and recorded on a strip chart recorder. The tape stain devices are good quantitative samplers of haze over an extended period of time. The variations of these devices employing radioactive sources as stain sensors are promising but are not, as yet, perfected to the point of being commercially available. They do appear to hold promise for future investigation.

The EPC (electric particle counter) [375] has a unipolar diffusion charger that is stable, controllable, and can classify particles with mobilities from 0.01 to 0.0002 (m per/v/cm) at aerosol flow rates up to 57 liters/min. Sufficient information is not available to assess this instrument with respect to haze sampling.

The Konitest [247] is a continuously functioning, recording flow sampler; similar to the conicycle, it is simultaneously used to measure the air or gas mixture passing through the instrument and its suspended dust content. Dust concentrations are established by measuring an electrical current generated by electric contact of the dust particles in the electric field. This instrument appears to show some promise for haze measurement but further investigation is required.

A cascade impactor has been developed [282] that can be used to monitor fine dust between 0.5-10 microns. Air is drawn through a slit and the particles are collected on a specially-positioned moving glass slide. The amount of dust deposited is measured photoelectrically.

Dust particles may be detected by acoustic phenomenon. In an instrument used by Langer [175], particles pass through the sensor, where they are accelerated to almost 100 m/sec and then suddenly projected into a wide exit cavity. The sensor detects particles down to 5 microns with no change in amplitude with particle size. Langer [176] describes experiments with the NCAR cloud nucleus counter. Filtered, humidified air (plus 10 cc/min of sampled air) is pulled through a Freon-cooled cloud chamber. Water vapor condenses on the condensation nuclei to form droplets. The droplets are counted acoustically at a rate of 10,000/min after they reach 20 microns. A glycol-water mixture flows over the walls of the cloud chamber to prevent frosting and to regulate chamber humidity. Langer [177] has also used this instrument mounted on an

aircraft for counting ice crystals. Bueker [28] describes a device for continuous gravimetric dust measurement by mechanical recorder. The change in fundamental frequency of a traverse oscillating band under vacuum is used to measure the amount of suspended dust. Band frequencies are excited and measured electrostatically by means of an ignition and measuring electrodes. This device is extremely interesting as a possible instrument of interest for haze measurement. However, more study is required before this device should be employed.

The scintillation spectrometer (SS) [23] automatically counts aerosol particles down to 0.01 microns, differentiates them by particle size, and permits their quantitative and qualitative analysis. The aerosol particles are individually introduced into a heating chamber. The heated particles emit a light pulse when the proper temperature is reached and the pulses are evaluated by an optical-electronic device. Sufficient information is not yet available concerning this device but it appears to show merit for future consideration for haze studies.

Ahlquist [2] discusses the use of a new instrument for evaluating the visual quality of air. The instrument is an adapted integrating nephelometer that records the volume scattering coefficient reliably over a month's operation. The sample air is drawn through the central chamber, 6 inches in diameter and 6 feet long, by a small vacuum cleaner. The particle-laden air is then irradiated by a Xenon flash lamp. The resulting light pulse is detected by a phototube and output from the phototube is amplified and fed into a specially designed peak reading voltmeter and recorded on a strip chart. This instrument may prove useful, but it is a specially-adapted device and should be investigated further.

A General Electric condensation nuclei particle detector has been used to detect particles too small to be observed by light

scattering particle counters [159]. This device operates on the principle of aspirating a gas sample into a humid chamber and, when equilibrium is reached, the humidified gas sample is expanded adiabatically. Any particles capable of nucleating in the resultant supersaturated mixture will produce water droplets in a concentration equal to that of the original nuclei. This type of instrument may also determine the size distribution of submicron aerosols when the device is used in conjunction with a diffusion battery.

Davis [52] has used the Pollak counter for checking the efficiency of installed filters and McGreevy [209] has adapted the Pollak counter for the purpose of obtaining a general picture of the size frequency distribution of an aerosol of Aitken nuclei. The method employs differential evaporation of the large and small water droplets formed at an expansion on different sized nuclei in the counter.

Gussman [117] also reports use of a condensation nuclei counter, based on a design by Pollak, that will accurately measure numbers concentration in the submicron particle-size range. This device is similar in operating principle to the G.E. unit but is manually operated.

A condensation nuclei counter, light scattering counter, and electrical particle counter have been combined by Peterson [236] to provide a device to monitor particle size over the range of 0.001 to 10 microns. The condensation nuclei counter is at present the most reliable device for sizing submicron particles. These instruments are commercially available and therefore are the choice instrument sizing haze particles below 1 micron.

C. Recommendations

1. To increase the reliability of aerosol identification, it seems necessary to combine various methods of direct and indirect monitoring (e.g., a polar nephelometer can be used together with a sampling device in overlapping aerosol-size range).

On the other hand, with respect to direct sampling and evaluation methods, several techniques exist that are currently considered to be of value only in the laboratory but which may be readily applied on a wider base. The diffusion battery and condensation nuclei counter are a prime example of techniques that can well be applied to the numbers and size-distribution quantitation of submicron aerosols in ambient atmospheres.

2. The future of holographic methods will depend on development of disdrometers using ultraviolet radiation (to lower down the left end of the size spectrum).

TABLE XII. Preliminary Classification and Characteristics of Haze Types.

Location	Chemical Composition	Origin	Effects	Particle Size Radius (μm)	Page
<u>Natural:</u>					
Ocean	NaCl plus some SO_4^{2-} , HCO_3^- , and other inorganic constituents of ocean water	Sea spray	Initiate formation of raindrops in clouds	≥ 1.0	Cascade impactor
					10 131
Continental arid regions	Soil minerals	Wind blown	Dust storms, soil minerals in ocean sediments	Depends upon sizes of mineral grains in soil; generally, $< 100 \mu\text{m}$	Cascade impactor, single particle counter
					19 131 123
Forests	Organic (terpenoid)	Terpenes from vegetation plus NO_2 and sunlight	Blue haze	~ 0.15	Scintillation spectrometer condensation nuclei counter
					137 138 15-19

Table XII (continued)

Location	Chemical Composition	Origin	Effects	Particle Size Radius (μm)	Page
<u>Natural</u> (continued):					
Volcanic eruptions	Silicate minerals H_2O (NH_4) ₂ SO_4	Plutonic	Clouds, dust veils, Lapilli showers, twilight effects	Submicrometer to boulders	131 123 130 19,20
<u>Man-Made:</u>					
Urban regions	Sulfates	Oxidation of SO_2 from combustion of coal and oil	"Acid aerosol" as in London-type fog	0.06-1.3	138 123 28-32
	Organic	Photochemical reactions, Olefins and NO_2 and sunlight	Photochemical smog	Submicrometer in dry atmospheres	138 35-43

Table XII (continued)

Location	Chemical Composition	Origin	Effects	Particle Size Radius (μm)	Page
<u>Man-Made (continued):</u>					
Urban regions	Trace metals	Combustion of all types, metal-lurgical processes	Pb-compounds may produce PbI_2 which may induce ice nucleation	0.1-0.2	138
					32
	NO_2	Combustion of all kinds but primarily auto-motive exhausts	Initiates photochemical smog formation in presence of sunlight; can contribute to brown color of urban haze	Gas	133
					43
Land and sea fogs	H_2O with traces of inorganic and organic materials	Droplets condensed on sea salt particles, combustion nuclei, and soil mineral grains	Visibility impairment	1-100	130 131 11,15

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